STABILIZING THE FERROELECTRIC PHASE OF KNO₃ THIN FILMS USING SUBSTRATE ELECTRODES

By

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Declaration

I hereby declare that this submission is my own work towards the PhD and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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Abstract

This research investigated the possibility of stabilizing the ferroelectric phase of KNO₃ thin films using substrate electrodes. The substrate electrodes used for this investigation were nickel (Ni), stainless steel (SS) and tantalum (Ta). The dip coating technique was used to deposit the films from the molten form of KNO₃. The ferroelectric properties of the films were characterized by means of polarization-voltage measurements, current density-voltage measurements, and dielectric constant temperature dependence measurements. From the results obtained, the effect of the different substrate electrodes on the KNO₃ thin film ferroelectric phase stability were determined. UV-Visible absorption spectroscopy was used to analyse the optical bandgap of KNO₃. An optical bandgap of 3.79 eV was obtained for the film deposited at 480.0 °C. The P-V hysteresis loops exhibited by the KNO₃ films deposited on the substrate electrodes and the temperature range over which the hysteresis loops extended revealed the possibility of stabilizing and extending the ferroelectric phase of KNO₃ thin films by means of an appropriate choice of substrate electrode. Well-defined hysteresis loops characterized the ferroelectric phase of the films deposited on SS and Ni but the films deposited on Ta exhibited unsaturated hysteresis loops. The Ni and SS substrate electrodes stabilized and extended the ferroelectric phase to 40.0 °C and beyond room temperature respectively. Ta extended the ferroelectric phase to about 50.0 °C. However, it did not stabilize the ferroelectric phase since it severely degraded polarization in the film a condition which led to poorly define hysteresis loops. The characteristic hysteresis loops exhibited by the different samples was attributed to the nature of the current (either displacive or leakage)

present in the sample. Displacive current is responsible for hysteresis loop formation while leakage current results in elliptical loop formation. The level of oxygen vacancies at the SS/KNO₃ and Ni/KNO₃ interface coupled with the electronegativity and d-shell occupancy of SS and Ni caused displacive current to be dominant in the films deposited on them. On the other hand, the films deposited on Ta suffered large leakage current effect due to the electronegativity and d-shell occupancy of Ta as well as the level of oxygen vacancies present at the Ta/KNO₃ interface. The dielectric constant behaviour of KNO₃ as temperature cooled through the paraelectric-ferroelectric phase revealed anomalies in the vicinity of the Curie point T_c. These dielectric constant temperature dependence curves obeyed the Curie-Weiss law just above T_c in the paraelectric region. The Curie point T_c and Curie temperature T_o were the same for all samples irrespective of the substrate electrode and this was evidence that the samples underwent a second-order transition. The films deposited on SS exhibited a shift in their inherent T_c from the reported range of between 120.0 °C and 124.0 °C to temperatures above 140.0 °C. The films deposited on Ni and Ta however exhibited no shift. The observed shift in T_c was attributed to strong polarization-strain coupling. The strain is however not due to misfit as a result of thermal stress and lattice misfit but rather due to lattice defects caused by the diffusion of Fe³⁺ ions into the deposited film layer during the deposition at elevated temperatures. These Fe³⁺ ions occupied a relatively smaller interstitial sites of KNO₃. This condition deformed the lattice of the films prepared on SS causing the development of strain in the film layer. This strain is believed to be the strain that coupled with polarization and caused the shift in T_c. The results obtained form this research have clearly demonstrated and proven the viability of stabilizing the ferroelectric phase of KNO3 thin films by means of an appropriate choice of substrate electrode. With respect to this research, austenitic stainless steel substrate electrode has stabilized and extended the ferroelectric phase of KNO₃ thin films beyond room temperature.

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List of Symbols and Acronyms

К	Dielectric constant	V	Unit cell volume
a	Lattice parameter	$\rho(r)$	Charge density
X	Dielectric susceptibility	P_i	Induced polarization
T _c	Curie point	τ	Electron affinity
T _o	Curie-Weiss temperature	δ_{ij}	Kronecker's delta
$\frac{1}{\varepsilon_r}$	Curie-Weiss temperature	Т	Temperature
σ_{f}	Thermal stress	p_i	Pyroelectric coefficient
K	constant defined as $\frac{\Delta T E_f}{(1 - v_f)}$	D_i	Dielectric Displacement vector
riangle T	Change in temperature	δ_{ij}	Kronecker's delta
E_{f}	Young's modulus	E_c	Coercive field
v_f	Poission's ratio	P_r	Remnant polarization
l_f	Misfit strain	P_e	Electronic polarization
$\frac{\partial D}{\partial t}$	Displacive current	α_e	Electronic polarizability
J_1	Leakage current	Pion	Ionic polarization
Φ	Schottky barrier height	α_{ion}	Ionic polarizability
W	Work function	P_o	Molecular polarization
D _i t	Density of the interface states	$lpha_o$	Molecular polarizability
Vo	Oxygen vacancy	P _{space}	Space charge polarization
P_s	Spontaneous polarization	α_s	Space charge polarizability
E_i	Applied Electric Field	α_{tot}	Total polarizability

- $\tan \delta$ Loss tangent
- ε_o Permittivity of free space
- ε_r Relative permittivity
- ε Absolute permittivity
- κ' Real component of the dielectric constant
- κ'' Imaginary component of the dielectric constant
- δ Dielectric loss angle
- C Capacitance
- *C*_o Standard Capacitor
- *p* Polarization moment
- *d* Distance between two charges
- q, Q Charge magnitude

MFM Metal-Ferroelectric-Metal structure

- Ni Nickel
- SS Stainless Steel
- Ta Tantalum
- TCC Thermal Coefficient of Capacitance
- TCD Temperature Dependence of Dielectric constant

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CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

Ferroelectricity, an electrical phenomenon by virtue of which certain materials exhibit spontaneous electric polarization even in the absence of an externally applied electric field, has immensely changed the face of technology in diverse and enormous ways since its discovery. By employing this phenomenon, several state-of-the-art device inventions have seen massive improvements with many more new ones emerging daily. The growing usage of materials exhibiting the phenomenon of ferroelectricity has generated extensive research interests for several scientists and engineers. Ferroelectricity has a wide and growing range of application areas. In most of these application areas, thin film forms are made use of (Muralt, 2007) because of the growing need for miniaturized devices.

Progress in this area of study over the past years has led to the discovery of a vast number of materials possessing ferroelectricity. One of such discovered material with very interesting ferroelectric properties is KNO₃. A metastable ferroelectric phase was discovered in its bulk form during cooling by Sawada et al. (1958). With the discovery of ferroelectricity in its thin film form (Nolta and Schubring, 1962), KNO₃ has since been seen as a viable material for device applications (Burfoot and Taylor, 1979). The thin film form of KNO₃ allows for low operating voltages (Scott, 2000) and fast switching responses (Scott, 2000; Kulkarni et al.,

1989b). Other qualities include non-volatility, fast switching responds, and high signal to noise ratio. In light of current research and technological needs, the thin film form of KNO_3 also makes way for miniaturization (Kumar and Nath, 2005; 2003).

A major setback regarding the use of ferroelectric KNO_3 in device applications is however in connection with the stability of its ferroelectric phase. It is required that a ferroelectric material which is viable for ferroelectric device applications exhibits a stable ferroelectric phase over the device's working temperature range. Thus, it is crucial that the thin film form of KNO_3 exhibit an excellent stable ferroelectric phase spanning low temperatures to high temperatures. This will allow for their use in device applications.

Over the past years, several attempts aimed at obtaining a KNO₃ thin film exhibiting a stable ferroelectric phase have been pursued by Nolta and Schubring (1962), El-Kabbany et al. (1989), Isaac and Philip (1991), Kumar and Nath (2003) and Dabra et al. (2009). This is premised on the many possible application areas a ferroelectric KNO₃ thin film is suited for most especially ferroelectric non-volatile memories (FeRAMs) (EerNisse, 1969; Scott et al., 1987; Wyncke and Brehat, 1987; Li et al., 2002a). Some of the explored options include applying hydrostatic pressure (Sawada et al., 1961), mixing of KNO₃ powder with starch (Davis and Adams, 1963), mixing of KNO₃ powder with silicon carbide (SiC) (Westphal, 1993). Zhang et al. (2004) report of substituting the NO₃⁻ radical of the KNO₃ compound with another radical, and hence forming a solid solution which stabilized the ferroelectric phase. Other attempts involve the formation of composites such as KNO₃-polyvinyl fluoride (PVF) (Kumar and Nath, 2005) and KNO₃-polyvinyldiene fluoride (PVDF) (Kumar and Nath, 2003).

Stabilization of the ferroelectric phase in thin films of KNO₃ at room temperature has been reported by Scott et al. (1987). According to this report, the phase stability is attributed to the existence of surface field effects. It is also believed that the presence of extraneous materials in KNO₃ can suppress the conversion of the ferroelectric phase to the paraelectric phase (Kumar and Nath, 2003), hence widening the temperature range over which the phase extends. For instance, Harris (1992) reports that when KNO₃ in potassium bromide (KBr) matrix was kept in a nonabsorbent liquid, it showed a very long stability of the ferroelectric phase at room temperature. Murugan et al. (1999) also report that by subjecting the sample to a higher preheating temperature and a higher cooling rate, the ferroelectric phase could be retained down to room temperature.

Among the many pursued attempts aimed at stabilizing the ferroelectric phase of KNO₃ thin films, there is no known attempt regarding the use of substrate electrodes. However, any device application that makes use of ferroelectric thin films necessarily incorporates the ferroelectric thin film layer in some form of device structure so that it can be coupled to an external circuitry (Paz de Araujo et al., 1996; Stucki, 2008). By this configuration, a KNO₃ thin film used in any device application is sandwiched between some device structure from which electrical contacts can be made. A substrate, can double as an electrode under which conditions a substrate electrode is referred to. This substrate electrode which forms an integral part of the device structure can alter certain qualities of the film and consequently influence the properties exhibited by the film. It can thus play a significant role with regards to the stability of the ferroelectric phase exhibited by KNO₃ thin films.

1.2 Objectives

This research sought to investigate the possibility of stabilizing the ferroelectric phase of KNO_3 thin films by means of a substrate electrode. The investigation was carried out using nickel (Ni), stainless steel (SS) and tantalum (Ta) metals as substrate electrodes. These metals were chosen for use as substrate electrodes because they are relatively cheap metals compared to platinum and gold which are usually the preferred choice of electrode when it come to device applications.

By attaining stability via the means of a substrate electrode, production cost and time will be reduce relative to the other investigated attempts aimed at achieving stability. Production cost will be reduced because only the pure KNO₃ other than KNO₃ mixed with some other material or compound will be required for device applications. Also, the time that will be used for the further processing of the KNO₃ powder and the other material or compound will be saved.

The characterizations used in this investigation included the following:

- Polarization-Voltage (P-V) measurements.
- Current density-Voltage (J-V) measurements.
- Dielectric constant temperature dependence.
- UV-Visible (UV-Vis) absorption spectroscopy.

The existence of ferroelectricity in the deposited KNO_3 thin films was investigated using the P-V hysteresis loop measurements. Though ferroelectric hysteresis behaviour occurs as a result of spontaneous polarization, hysteresis phenomenon may also develop as a result of

artifacts (Dawber et al., 2005; Rabe et al., 2007). On this basis, current density-voltage (J-V) measurements were used to verify the source of observed hysteresis behaviour exhibited by the samples. The transition temperature as well as the features associated with paraelectric to ferroelectric transitions of ferroelectrics were also investigated using the temperature dependence behaviour of the dielectric constant of the ferroelectric KNO₃ layer. Wide bandgap semiconductor materials interact with metals at the interface when the two materials are in contact. Since a ferroelectric can be semiconducting, the optical bandgap of the KNO₃ used in this work was investigated using optical absorbance spectrum obtained via UV-Vis absorption spectroscopy.

1.3 Thesis Layout

Chapter 1 introduces the reader to the research motivation and objective, followed by Chapter 2 with a review on KNO_3 . The chapter progresses further with a discussion on ferroelectric interaction with substrate electrode which then leads to a discussion on the substrate electrode materials chosen to undertake this study. The phenomenon of ferroelectricity as well as the material properties responsible for the development of this phenomenon is also discussed. A discussion is also carried out on the phenomenological theory which governs this phenomenon of ferroelectricity. This chapter also contains a discussion on some optical constants determination. Finally in this chapter, the deposition techniques used in thin film depositions are presented focusing on the dip coating approach. Chapter 3, deals with the experimental details of this research. The early sections of this chapter present the materials used in this work and then describe how the samples used for the different characterizations are prepared. This chapter also presents a discussion of a designed and constructed dip coating unit employed for the deposition of KNO₃ thin films used in this study. The rest of

this chapter then discusses the measurement approaches utilized to obtain the results of this work. Chapter 4, presents the results of the various characterizations undertaken. Chapter 5, discusses the results obtained and Chapter 6 draws the conclusions of the work and presents the necessary recommendations for future investigations.

CHAPTER 2

LITERATURE REVIEW

2.1 Potassium Nitrate

Potassium nitrate (KNO₃), is an inorganic material discovered to exhibit the phenomenon of ferroelectricity since 1958 (Sawada et al., 1961). It can be classified to belong to the non-oxide ferroelectric family (Martienssen and Warlimont, 2005) and has a crystal structure based on stacking of triangular NO_3^- units and K⁺ ions (Rabe et al., 2007). It is known to possess a low melting point of 334 °C. It can melt to liquid without decomposing and thus, remains stable in air up to at least 530 °C. However, it begins to decompose near 650 °C when heated in air (Stern, 2001). KNO₃ can exist in several polymorphic forms and has its ferroelectric phase associated with only one of these polymorphic forms (Kumar and Nath, 2005; Aydinol et al., 2007). It is classified as an order-disorder ferroelectric (Hardy and Lu, 1991) and undergoes a first-order ferroelectric transition in the bulk but a second-order transition in thin film form (Nolta et al., 1965; Rapoport and Kennedy, 1965; Chen and Chernow, 1967). Its ferroelectric phase is characterized by a true hysteresis field threshold, a modest spontaneous polarization, a very low permittivity, a high resistivity and a low loss which are characteristic of an ideal electrical switch (Sawada et al., 1961; Nolta and Schubring, 1962; Aydinol et al., 2007). As mentioned in Chapter 1, it also has excellent memory characteristics such as non-volatility, fast switching responds, high signal to noise

ratio as well as radiation hardness (Kulkarni et al., 1989a) and is therefore considered a promising material for binary non-volatile memory devices (FeRAMs) (Scott et al., 1987), ferroelectric transistors (Li et al., 2002a), parametric amplifier (EerNisse, 1969), ferroelectric capacitors, switching devices (Paz de Araujo et al., 1996) and thermal detection devices (Wyncke and Brehat, 1987).

2.1.1 Room Temperature Unit Cell

Solid KNO₃ exits in three well-known phases at atmospheric pressure (Strømme, 1969). The phase that exists at room temperature has an orthorhombic aragonite (*Pmcn*) structure (Nolta et al., 1965) (see Figure 2.1). This phase is usually referred to as phase II or α -phase. The structural configuration of this phase comprises complex NO₃⁻ ions which lie on the x - y plane as shown in Figure 2.2a and simple K⁺ ions which lie on the y - z plane as shown in Figure 2.2b. KNO₃ crystallizes in this phase with four formula units (Diéguez and Vanderbilt, 2007).



Figure 2.1: Unit crystalline cell of potassium nitrate (after Eringen (1999)).



Figure 2.2: Project of the KNO_3 unit crystalline cell in the yz-plane (a) and the xy-plane (b) after (Eringen, 1999).

When the bulk form of KNO₃ is heated, its room temperature α -phase undergoes a transformation at ≈ 128 °C to another phase designated as phase I or β -phase (Strømme, 1969; Aydinol et al., 2007) which has a trigonal ($R\bar{3}m$) structure with the nitrate groups orientationally disordered in calcite-type positions (Strømme, 1969; Aydinol et al., 2007). Upon cooling at atmospheric pressure from a higher temperature, phase I does not transform back to phase II; rather, there exists a narrow window of temperature between ≈ 124 °C and 110 °C within which a ferroelectric phase composed of a five-atom rhombohedral R3m symmetry cell appears (Hardy and Lu, 1991; Diéguez and Vanderbilt, 2007; Zhang et al., 2004; Erdinc and Akkus, 2009). This phase is usually known as phase III or γ -phase and has the nitrate groups ordered in aragonite-type positions (Strømme, 1969; Aydinol et al., 2007). Phase II reappears upon further cooling attaining its orthorhombic structure again. This interesting phase transformation sequence exhibited by bulk KNO₃ during heating and cooling under atmospheric pressure is illustrated in Figure 2.3.



Figure 2.3: Phases of solid KNO₃.

2.1.2 Bonding in KNO₃

 KNO_3 possesses mixed covalent and ionic bonding. An electronic structure and orbital hybridization analysis of the constituent atoms have revealed the existence of covalent interaction within the N–O bond of the NO_3^- group atoms whiles ionic interactions occur between the negatively charged NO_3^- group and the K⁺ cations. As a consequence of the ionic bonding present in this material, the cations form a layer of triangular networks above and beneath the groups (Aydinol et al., 2007).

2.1.3 KNO₃ Symmetry Considerations

The origin of ferroelectricity in KNO₃ arises from the shift in the nitrate (NO₃⁻) groups from the centre of the unit cell along the *c*-axis during transition (Murugan et al., 1999). The NO₃⁻

groups therefore jump between two equivalent positions following the reversal of the external electric field (El-Kabbany et al., 1995). The unit cell of ferroelectric KNO₃ (phase III) as already mentioned is a five-atom rhombohedral cell with R3m symmetry. Figure 2.4 is a depiction of the top and side views of a fifteen-atom conventional hexagonal cell for ferroelectric KNO₃ in the ground state with the coloured lines representing the negative polarization.



Figure 2.4: Top and side views of the fifteen-atom conventional hexagonal cell for ferroelectric KNO_3 ; the blue lines represent the equivalent five-atom rhombohedral cells (Diéguez and Vanderbilt, 2006).

This structure comprises stacked planes consisting of alternating K^+ atoms and NO_3^- groups. The K^+ plane is however not equidistant from the NO_3^- plane above it or the one below it. The structure instead, adopts a polar system. In this polar system, the distance between a given K^+ atom and its six O^{2+} second-neighbours in the NO_3^- plane below it is reduced at the expense of increasing the distance between this same K^+ atom and its three O^{2+} first-neighbours in the NO_3^- plane above it. The blue lines indicate the equivalent five-atom
rhombohedral cells and the far right structure depict the top view of the same structure clarifying the near neighbour environment of a K atom. Neighbours in the plane above and below are indicated with black and blue lines respectively; the first K–O neighbours are drawn as dashed lines while the second K–O neighbours are designated by dotted lines (Diéguez and Vanderbilt, 2006). The nitrate orientation is taken to be 0°. Experimentally, the optimum stacking occurs when every K⁺ plane is roughly three times closer to the NO₃⁻ plane below it than to the one above (Diéguez and Vanderbilt, 2006).



Figure 2.5: Top and side views of the fifteen-atom conventional hexagonal cell for ferroelectric KNO_3 in the ground state with positive polarization (Diéguez and Vanderbilt, 2006).

For the condition of a reversal of polarization which is a confirmatory feature of the existence of ferroelctricity, there exists a polarization-reversal structure having the same energy. However in the resulting structural configuration, the K⁺ planes are closer to the $NO_3^$ above them than to the one below. In addition, the polarization reversal is accompanied by an NO_3^- rotation in order to preserve symmetry (Diéguez and Vanderbilt, 2006). The resulting structure then becomes like what is shown in Figure 2.5. The blue lines indicate the equivalent five-atom rhombohedral cells and the far right structure shows the top view of the same structure clarifying the near neighbour environment of a K atom. Neighbours in the plane above and below are indicated with black and blue lines respectively; the first K–O neighbours are shown as dashed lines while the second K–O neighbours are indicated by dotted lines.



Figure 2.6: Top and side views of the fifteen-atom conventional hexagonal cell for ferroelectric KNO_3 in a metastable paraelectric state (Diéguez and Vanderbilt, 2006).

An intermediate paraelectric configuration existing between these ferroelectric structural configuration has an R32 symmetry type as illustrated in Figure 2.6. Then K⁺ planes are equidistant from the NO₃⁻ plane above and below it. Each K⁺ atom has six equidistant first-neighbours. The equivalent five-atom rhombohedral cells in this configuration is indicated with blue lines and the far right structure shows the top view of the same structure clarifying the near neighbour environment of a K atom. Neighbours in the plane above and below are indicated with black and blue lines respectively; both the first and second K–O neighbours are drawn as dotted lines because the K⁺ planes are equidistant from the NO₃⁻

plane above and below it. This structure is however not stable in nature but corresponds to the saddle point on the energy surface connecting the degenerate minima. The nitrate groups in this configuration correspond to 30 ° rotation (Diéguez and Vanderbilt, 2006).

2.2 Substrate Electrode

A substrate provides mechanical support for a deposited film layer. In selecting a material to be used as substrate, some factors such as thermal conductivity and thermal coefficient of expansion are considered. When dealing with non-metallic substrates, consideration is also given to the the dielectric constant of the substrate. The dielectric constant of non-metallic substrates can considerably determine the capacitance associated with a deposited film. Thermal conductivity considerations become prime when dealing with applications in which circuits generate significant amount of heat. With regards to strain related effects, the thermal coefficient of expansion of the substrate becomes a very relevant consideration (Kasap, 2006). A substrate electrode is so named when the substrate also serves as the electrode to the prepared thin film layer (Ionescu et al., 2010).

Electrodes play a major role in determining device properties and performance. Electrodes can modify a film's microstructure and in some cases directly control film properties. In choosing an electrode material, the following criteria are taken into consideration. The material must be sufficiently low in resistance to allow for a high electrical conductivity. It is also required that the material be chemically compatible with the ferroelectric material so that it does not react with the deposited film. The material must also be able to act as a diffusion barrier for oxygen to prevent the accumulation of oxygen at the metal/ferroelectric interface. It is also necessary that the electrode material provides adhesion for the film

material. Other criteria include the morphological stability of the material under the particular processing condition, its interfacial electronic properties and also its ability to control the film's microstructure and orientation (Paz de Araujo et al., 1996).

Noble metals such as platinum (Pt), gold (Au), silver (Ag) are usually chosen for electrode application though Pt is preferred above the other noble metals because it does not react with perovskites during processing. A range of other metals such as electroless nickel, stainless steel and titanium are also used (Paz de Araujo et al., 1996). In this work. nickel, stainless steel and tantalum elemental metal electrodes are used as substrate electrodes.

2.2.1 Nickel

Nickel (Ni) is an important and very widely used electrode metal in the electronic industry (Yang et al., 2010). Ni is a transition element which exhibits both ferrous and nonferrous metal properties. Nickel is a hard silvery-white metal that is extremely shiny and malleable. It is also ductile and can easily be stretched into wires and sheets. It can withstand very high and very low temperatures and has a work function of 5.0 eV. Nickel is only one of three naturally occurring elements that is strongly magnetic (Stimola, 2007). It has a Curie temperature of 355 °C. It possesses a face centred cube as unit cell and has a lattice parameter of 0.352 nm giving an atomic radius of 0.124 nm at room temperature. Chemically, nickel is a relatively unreactive element. At room temperatures, it becomes more active. Its melting point is 1453 °C and its boiling point is about 2835 °C. It is used in several applications including electrical and electronic applications. Nickel is relatively cheap compared to platinum and gold. It is used in this work because of its relatively high work function and its

good electrical conductivity.

2.2.2 Stainless steel

Stainless steel as one of the most widely used alloys in the world is gaining attraction day by day in both commercial and research aspects (Wijesinghe, 2005). It finds application in the area of architecture, marine engineering, medical equipment, chemical engineering, food and drink production and distribution, domestic and catering applications. It is a hard alloy that is very resistant to corrosion, oxidation or rusting. The corrosion resistance of stainless steel arises from a 'passive' chromium-rich oxide film that forms on the surface. It is an alloy of iron consisting of more then 12 % to 13 % chromium . Various alloying elements are added to stainless steels, each for a specific reason: chromium addition is quite obvious without which the word 'stainless steel' would not exist; nickel is added as an austenitic former and molybdenum particularly for enhanced localized corrosion resistance (Wijesinghe, 2005). Out of the different classes of stainless steels, austenitic stainless steels claim more than 70 % of the production. Due to the flexibility of both their metallurgical and mechanical properties, austenitic stainless steels provide a blend of corrosion resistance, durability and ease of manipulation. Stainless steel is strong with a relatively high thermal conductivity. It is also a good electrical conductor (Kasap, 2006) possessing a work function of 4.5 eV. It is chosen as a substrate electrode material in this research because of its good electrical conductivity, its relatively high work function as well as its relatively low cost in comparison to the noble metals.

2.2.3 Tantalum

Tantalum is a soft, malleable and remarkably ductile transition metal that is at the same time very tough with high mechanical strength. It is highly conductive of heat and electricity and has a melting point of 2996 °C and a boiling point of 5425 °C. The metal is renowned for its resistance to corrosion and also its inertness to attack by most acids even at temperatures up to 150 °C; only fused alkalis, hydrofluoric acid and a mixture of nitric and hydrochloric acids can slowly dissolve it. Its electrical properties remain stable over a wide range of temperatures starting from -55 °C to 125 °C. It has a work function of 4.1 eV. At room temperature, tantalum has a body centred cubic crystal lattice structure and a lattice parameter of 0.330 nm. It is used in capacitors and other electronic equipment. The advantage of using tantalum lies not only in its good electrical conductivity which is stable over a wide range of temperature but also in its high specific gravity that enables miniaturization of the capacitors into low-volume high-performance equipment (Chatterjee, 2007). It is also relatively low in cost compared to the noble metals.

2.3 Ferroelectric-Substrate Electrode Interaction

In ferroelectric thin film applications, the film is integrated into the device. This integration results in the creation of an interface between the film and its substrate and between the film and one or more electrodes in contact with the ferroelectric film layer. For instance, the capacitor device structure which is the fundamental fabrication idea implemented in many ferroelectric device applications always comprises interfaces (Stucki, 2008). The interface existing between the thin film and its substrate as well as the electrode can be a very important

factor in determining the electrical properties of the film (Paz de Araujo et al., 1996).

2.3.1 Electrical Contact Effects

The electrical contact provided by an electrode to a device is generally expected to be an ideal contact that in itself does not alter the electrical characteristics of the device. In most devices, an ohmic or non-rectifying contact is required (Sze and Ng, 2007). Most often the basic nature of the interface between two materials and in particular between a metallic conductor and a dielectric or semiconductor results in a non ohmic contact. This causes the development of asymmetric device characteristics due to self-biased heterojunction effect at the ferroelectric-electrode interface (Kalkur et al., 1990). When a metal and a semiconductor are brought together, a non-ohmic contact can occur. Since dielectrics and ferroelectrics are wide bandgap semiconductors, their contact with metals can possibly result in non-ohmic contacts. A non-ohmic rectifying contact is formed when the Fermi levels of both the metal and semiconductor align and establish thermodynamic equilibrium through the transfer of electrons from the semiconductor conduction band into the metal. This condition leaves positively charged donor impurity atoms in the semiconductor. A space-charge region corresponding to the zone depleted of electrons, is, therefore, formed in the semiconductor near the interface with the metal. This layer of space-charge at the interface supports a potential drop called diffusion voltage. The energy difference or barrier for carrier injection from the metal to the semiconductor is termed Schottky barrier. Conduction across a Schottky barrier is generally rectifying (Colinge and Colinge, 2002; Paz de Araujo et al., 1996). Ohmic contacts on the other hand do not significantly change the characteristics of a device. With ohmic contacts, there is virtually no potential barrier between the metal and the semiconductor and electrons can freely flow through the contact (Colinge and Colinge,

2002; Paz de Araujo et al., 1996).

2.3.2 Effects of Diffussion and Reactions

An electrode can alter the behaviour of a ferroelectric material by diffusing into and chemically reacting with the ferroelectric thus changing the chemical nature of the material. Cations can diffuse from the electrode into the ferroelectric causing doping of the material. The interface of the electrode can also be oxidized through the gettering of oxygen from the ferroelectric as well as the diffusion of oxygen through the electrode. Layers of differing phase or differing stoichiometry formed by diffusion and reaction of species at an electrode-ferroelectric interface affect the overall dielectric properties of the entire device (Paz de Araujo et al., 1996).

2.3.3 Effects of Film-Substrate Mismatch

Ferroelectric behaviour is also influenced by a substrate electrode through the introduction of strain into the material. This consequently causes spontaneous polarization of the ferroelectric. Strains can be imparted into thin films through differences in lattice parameters (Lang, 2006) and as well as through thermal expansion coefficient differences between the film and the underlying substrate (Liu and Santos, 1999). Strong polarization-strain coupling can result in change in the paraelectric-ferroelectric transition temperature, piezoelectric properties and electro-optic properties when the mechanical boundary conditions of a ferroelectric are altered. Strain-induced enhancements in transition temperature have been observed for the phenomenon of ferromagnetism and superconductivity (Schlom et al., 2007). Owing to the strong coupling between strain and polarization, transition temperature shifts of hundreds of degrees are expected and have been observed in strained ferroelectric thin films (Schlom et al., 2007).

2.3.3.1 Lattice Mismatch

Lattice mismatch between substrate and film is known to influence strongly the properties of thin films. Large strain in the plane of the film can occur due to this type of mismatch between a substrate and the deposited thin film. The existence of such a mismatch causes the the film to experience either a compressive or tensile strain which can influence the direction of polarization. The polarization may for instance lie in the film layers or may have a component perpendicular to such layers (Lang, 2006; Diéguez et al., 2004).

Lattice mismatch and/or thermal expansion mismatch result in misfit strains. Lattice misfit (or misfit strain) has been identified to significantly increase the phase transition temperature of BaTiO₃ as reported by Choi et al. (2004) and Yanase et al. (1999) and Lead Zirconate Titanate (PZT) thin films as observed by Cheng et al. (2006). The restraint of the misfit strain due to the rigidity of the substrates may enhance the polarization of the ferroelectric state, increase the Curie temperature and even cause a thin film of first-order ferroelectric material to undergo a second-order transition (Zheng et al., 2007). Lattice misfit l_f (Sze and Ng, 2007) is defined in terms of lattice parameters of the film layer a_f and the substrate a_s as

$$l_f = \frac{a_f - a_s}{a_f} \tag{2.1}$$

2.3.3.2 Thermal Stress

Films deposited at elevated temperatures and then cooled to room temperature get thermally stressed. Thermal effects provide important contribution to film stress (Ohring, 1992). For the film-substrate combination subjected to a temperature difference $\triangle T$, the film and substrate strain are respectively given as

$$\varepsilon_f = \alpha_f \bigtriangleup T + F_f \frac{(1 - \nu_f)}{E_f d_f w}$$
(2.2)

$$\varepsilon_s = \alpha_s \bigtriangleup T - F_f \frac{(1 - \nu_s)}{E_s d_s w}$$
(2.3)

But the strain compatibility requires that $\varepsilon_f = \varepsilon_s$; hence, the thermal mismatch force F_f becomes

$$F_f = \frac{w(\alpha_s - \alpha_f) \Delta T}{\frac{(1 - \nu_f)}{d_f E_f} + \frac{(1 - \nu_s)}{d_s E_s}}$$
(2.4)

If $\frac{d_s E_s}{(1 - v_s)} \gg \frac{d_f E_f}{(1 - v_f)}$ the thermal stress in the film is given as

$$\sigma_f(T) = \frac{F_f}{d_f w} = \frac{(\alpha_s - \alpha_f) \triangle T}{(1 - \nu_f)} E_f$$
(2.5)

Films prepared at elevated temperatures will be residually compressed when measured at room temperatures ($\Delta T = 0$) if $\alpha_s > \alpha_f$. In this case, the substrate shrinks more than the film. Since the film-substrate system must contract to a fixed amount, a compromise is reached. The substrate is prevented from fully contracting while the film is hindered from shrinking. The substrate is thus placed in tension whilst the film is consequently forced into compression (Ohring, 1992). The greater the thermal mismatch between the film and the substrate, the stronger the stress generated in the film.

2.4 Ferroelectricity

Ferroelectricity was discovered by Joseph Valasek in 1921 while working on Rochelle Salt (Safari et al.; Jie, 2006; Valasek, 1921; Grishin, 2005). Rochelle Salt is a colourless crystalline compound with a chemical formula of $KNaC_4H_4O_6 \cdot 4H_2O$ (Kao, 2004). It is a double tartrate of sodium and potassium crystallizing with four molecules of water in the orthorhombic crystal system. This phenomenon was first named as Seignette electricity in honour of the man who first discovered and developed Rochelle salt (Seignette). The name was later changed to its present name (ferroelectricity) to depict its characteristic behaviour. The discovery of ferroelectric phenomena in Barium titanate (BaTiO₃) in the early 1950s changed the face of research in this field and led to the wide spread use of BaTiO₃ based ceramics in capacitor applications and piezoelectric transducer devices.

Materials that exhibit the features of ferroelectricity are referred to as ferroelectrics or ferroelectric materials. The term 'ferroelectricity' was coined only because of the strict analogy between the electrical behaviour of such materials and the magnetic behaviour of ferromagnetic compounds (Surowiak, 2006). Irrespective of the many similarities between ferroelectrics and ferromagnetics such as spontaneous polarization, domain structure, hysteresis and Curie temperature, these two phenomena totally differ from each other. For instance the paraelectric to ferroelectric phase change that occurs at the Curie point in ferroelectrics involves the rearrangement of ions and change of crystal symmetry whiles in the case of ferromagnetic materials, the transition between the spontaneously magnetized and magnetically disordered states that occurs at the Curie point does not involve a change

in crystal structure. Ferroelectrics also possess spontaneous electric polarization due to a change in the crystal structure to a noncentrosymmetric structure in the ferroelectric phase while spontaneous magnetization of ferromagnets is due to unpaired and unsaturated electron spins. Above the Curie point, spontaneous electric polarization in ferroelectrics disappears since the crystal structure changes to a centrosymmetric system while individual magnetic moments of unpaired electron spins do exist, but are randomized and cancel one another completely due to thermal motion in ferromagnetics (Cao, 2003). The prefix 'ferro' in the designation ferroelectricity is derived from 'ferum' which means iron in Latin. However, the 'ferro' prefix is something of a misnomer (Rabe et al., 2007) since the presence of the iron is not a necessary condition to qualify a material as ferroelectric (Spartak, 2009). Recent advancements in these two fields of studies has resulted in the grouping of both classes of materials under the banner of 'ferroic' materials.

Ferroelectrics are a special group of dielectric materials which exhibit the phenomenon of ferroelectricity. This phenomenon is characterized by the possession of two or more orientational states in the absence of an externally applied electric field. It must be emphasized that the reversibility of these discrete stable or metastable state by an appropriately oriented applied electric field qualifies a material to be ferroelectric. These states possess nonzero electric polarization referred to as "spontaneous" polarization P_s in zero applied electric field (Rabe et al., 2007). By coupling the applied field to the polarization, the applied electric field changes the relative energy of the system. In the case of a normal dielectric, charge centres of the positive and negative ions become displaced from their original position when an external electric field is applied resulting in polarization. The developed polarization however disappears upon the removal of the applied electric field (Koo, 2003).

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Ferroelectric materials are predominately characterized by ionic bonds. The ions within the atomic lattice orient into a configuration that minimizes the internal energy of the system. This orientation is strongly dependent on temperature and composition. Slight changes in the composition near the morphotropic phase boundary (MPB) can change the crystal structure into either a tetragonal, monoclinic, orthorhombic or rhombohedral phase (Oates, 2004). Ferroelectrics exhibit ferroelectricity only within a certain temperature range after having gone through a phase transformation. As a ferroelectric material cools through the phase

transformation temperature, spontaneous strain and polarization develop at the unit cell level. This is illustrated in Figure 2.7.



Figure 2.7: The development of spontaneous polarization P_s and strain in a unit cell from cubic (left) to tetragonal (right). P_s is induced as the body centred atom shifts from its central position.

Ferroelectrics belong to a larger group of crystals which exhibit the piezoelectric phenomenon. This phenomenon is defined as the ability of a crystal to develop electric charges proportional to an applied mechanical stress. A converse effect occurs where a

piezoelectric crystal deforms in response to an applied voltage. Piezoelectric effect is linear and it is only those piezoelectric materials that show spontaneous polarization that are ferroelectric. The existence of spontaneous polarization in a material is detected by the observation of charge flows to and from the crystal on change of temperature. This results in the appearance of charges on the crystal surface. This phenomenon of the appearance of charge on a crystal surface on temperature change is known as pyroelectric effect. Pyroelectrics show spontaneous polarization within a certain temperature range. For a pyroelectric to be ferroelectric, the magnitude and the direction of the spontaneous polarization developed in the pyroelectric material must be reversible by an externally applied electric field. All ferroelectric materials have a transition temperature called Curie point designated T_c . P_s falls to zero at the Curie point. A detailed treatment of elements of geometry and symmetry that categorizes a material as piezoelectric, pyroelectric and ferroelectric is done in section 2.12 on page 48.

2.5 Dipoles and Dipole moments

A dipole can be considered to be a fundamental element responsible for ferroelectricity. It is formed when charges of equal magnitude q, but opposite in polarity separate (Webb, 2003). With the exception of polar molecules, dipoles are generally absent in dielectrics and for such dielectrics, dipoles only develop after an external electric field has been applied. The applied electric field, E_i (Vm⁻¹) (i = 1, 2, 3) polarizes the material by separating the positive and negative charges (Damjanovic, 1998). Normally, any collection of positive charges in the absence of an applied field has a centre that coincides with the centre of a collection of negative charges. However, an atom as a whole may be charged because the total negative charge may not have the same magnitude as that of the positive charge in which case the total charge which is the sum of the positive and negative charges is either positively biased or negatively biased. Such an atom is called an ion and the solid composed of these atoms becomes an ionic crystalline solid.

Ionic crystalline solids are made up of more than one type of ion arranged in a regularly repeating structure (a crystal lattice). Each ion can be considered to have a charge at its centre and the total charge of all the ions add up to zero. The charge centres are also normally arranged in a way that cancels overall. In such a case there are no dipoles and this is the natural arrangement of dielectrics (Webb, 2003). Nevertheless, it turns out that in nature there exist certain kinds of dielectrics in which the natural balance does not cause charge cancellation at each ion site but results in dipole formation (Webb, 2003). These dipoles then result in dipole moments p according to the equation 2.6 where d is the separation between the charge centres.

$$p = qd \tag{2.6}$$

2.6 Polarization

All dipole moments add up to give a net electrical polarization vector P (Cm⁻²) defined as dipole moment per unit volume. This polarization vector, describes the macroscopic manifestation of charge separation which is evident via the presence of surface charges (Damjanovic et al., 2006; IEEE, 2003). It is the key concept of ferroelectricity. Equation 2.7 typically describes the polarization for a system composed of individually distinguishable elementary dipoles.

$$P = \frac{qd}{V} \tag{2.7}$$

where V is the volume of the unit cell (Rout, 2006). For most dielectric crystals that exhibit pyroelectric effect, such elementary dipoles cannot be individually distinguished and the material is better represented by an assembly of point charges (IEEE, 2003). Polarization, *P* in a perfect dielectric composed of a system of bound electric charges of charge density $\rho(r)$, is thus given by equation 2.8.

$$P = \frac{1}{V} \int_{V} r\rho(r) dV$$
(2.8)

where *V* is a representative volume containing all of the species of interest and *r* is position. It is seen from equation (2.8) that *P* is independent of the spatial reference frame if the volume considered is electrically neutral. This is automatically ensured for a system of elementary dipoles when *P* is simply the dipole moment averaged over a unit volume (IEEE, 2003). It has been observed that even if the assembly is neutral as a whole, the polarization defined by equation 2.8 depends on the shape of the sample (Aizu, 1970; 1972).

Polarization can be induced in a dielectric material of any symmetry when an electric field is applied. This induced polarization P_i in a linear polarizable dielectric material manifests as surface charge. Equation 2.9 describes the relationship between the applied electric field and the induced polarization.

$$P_i = \chi_{ij} E_j \tag{2.9}$$

where χ_{ij} is the electric susceptibility tensor of the dielectric medium. The total surface charge density induced in the material by the applied field is given by the dielectric displacement vector D_i (Cm⁻²) (Damjanovic et al., 2006). This vector is a combination of the charges associated with the polarization of the material P_i and the charges created by the polarization of free space $\varepsilon_o E_i$. Therefore, D_i , the magnitude of which is equal to the charge density when an external electric field E_i is applied is expressed as

$$D_{i} = \varepsilon_{o}E_{i} + P_{i} = \varepsilon_{o}E_{i} + \chi_{ij}E_{j} = \varepsilon_{o}\delta_{ij}E_{j} + \chi_{ij}E_{j} = (\varepsilon_{o}\delta_{ij} + \chi_{ij})E_{j} = \varepsilon_{ij}E_{j}$$
(2.10)

where $\varepsilon_{ij} = \varepsilon_o \delta_{ij} + \chi_{ij}$ represents the dielectric permittivity of the material and δ_{ij} is Kronecker's delta (Damjanovic et al., 2006). ($\delta_{ij} = 1$ for i = j and $\delta_{ij} = 0$ for $i \neq j$).

For most ferroelectrics, $\varepsilon_o \delta_{ij} \ll \chi_{ij}$ therefore $\varepsilon_{ij} \approx \chi_{ij}$. For ferroelectrics, the polarization arise both from the polarizability P_e of the ferroelectric in the presence of a field and from the spontaneous alignment of ferroelectric dipoles P_{s_i} . Thus, in this case the electrical displacement D_i becomes (Hong, 2004)

$$D_i = \varepsilon_o E_i + \chi_{ij} E_j + P_{s_i} = \varepsilon_{ij} E_i + P_{s_i}$$
(2.11)

Polarization of a system results from several electric polarization mechanisms. The short-range transport of charges which subsequently results in electrical polarization occurs in four distinct mechanisms namely electronic, ionic, dipolar and space charge polarization.

2.6.1 Electronic Polarization

Electronic or atomic polarization (P_e) with polarizability α_e is a property of all dielectrics (Kao, 2004). It is as the result of a shift in the relative positions of the electron cloud and the atomic nuclei of an atom or and ion under the influence of an applied electric field to form an electric dipole. On a macroscopic scale, the physical dimension of a system

becomes altered owing to atomic displacement (Waser et al., 2005). These atomic dipoles resonate back and forth in step with the frequency of the alternating field when an AC field is applied. This polarization occurs instantaneously, in response to light electromagnetic field frequencies $\approx 10^{15}$ Hz, since the electrons have a very high natural frequency $\approx 10^{16}$ Hz. Electronic polarization, being resonant in nature, is independent of temperature. Perfect elemental single crystals, such as diamond and silicon, possess only electronic polarization (Cao, 2003). This polarization mechanism is elastic hence a system which undergoes atomic polarization returns to its original position after the field is removed. This polarization mechanism is observed over a wide spectral range (Waser et al., 2005) and is illustrated in Figure 2.8 (Cao, 2003). This effect occurs in all materials because all materials contain atoms. The magnitude is however small because of very small distance of separation between the positive and negative charge centres. Typical displacements are ≈ 1 Å giving a dipole moment of $\approx 1.6 \times 10^{-37}$ Cm. Electronic polarization is the only possible mechanism in pure materials that are covalently bonded and does not contain permanent dipoles for example silicon and diamond (Carter and Norton, 2007).



Figure 2.8: Electronic polarization mechanism. Atomic nuclei are represented by blue pattern and Electron cloud is represented by red pattern.

2.6.2 Ionic Polarization

Ionic polarization (P_{ion}) with polarizability α_{ion} , is the displacement of negative and positive ions toward the positive and negative electrodes respectively (Cao, 2003) upon the application of an external field resulting in the creation of temporary induced dipoles. Ions are much more massive than electrons, thus, ions cannot become polarized as rapidly as electrons. Ionic polarization is limited to a maximum frequency of $\approx 10^{13}$ Hz. This value is below the frequency of visible light. Therefore, the electromagnetic field of visible light cannot produce ionic polarization, as it does electronic polarization. Like electronic polarization, ionic polarization is resonant in nature and is independent of temperature. Ionic polarization occurs in compounds in which chemical bonds are not 100 % covalent (Cao, 2003). Figure 2.9 illustrates this mechanism.

E = 0	$E \neq 0$
Unpolarized State + - + - + - + - +	Polarized State + - + - + - + - +-
- + - + - + - + -	-+ -+ -+ -+
+ - + - + - + - +	+- +- +- +- +-
- + - + - + - + -	-+ -+ -+ -+
+ - + - + - + - +	+- +- +- +- +-
- + - + - + - + -	-+ -+ -+ -+

Figure 2.9: Ionic polarization mechanism.

2.6.3 Molecular Polarization

Molecular, dipolar or orientational polarization (P_o) with polarizability α_o , occurs in materials consisting of polar molecules or unit cells only. In polar molecules, the centre of positive charges do not coincide with that of negative charges. Thus, an electric dipole is present in each molecule or unit cell. Molecular polarization is permanent, since it is inherent in the molecular structure. These dipoles are randomly oriented but can be aligned in the presence an electric field as depicted in Figure 2.10. Furthermore, the polar molecules can flip back and forth in response to an AC field. The maximum frequency of response varies significantly from one polar dielectric to another depending on the size of molecule. It is however always less than that for the electronic and ionic polarization and is typically less than 10 ¹⁰Hz. Unlike the electronic and ionic polarization, dipolar polarization is temperature dependent (Cao, 2003). 5



Figure 2.10: Molecular polarization mechanism.

2.6.4 Space Charge Polarization

Space charge or interfacial polarization (P_{space}) with polarizability α_s , is a short-range electrical conduction. A space charge develops when there is a local conduction that is, a drift of mobile ions or electrons within a dielectric. It can exist in dielectric materials which show spatial inhomogeneities of charge carrier densities. Such a local conduction stops at a barrier

or an energy potential, such as grain boundaries. Due to the nature of diffusion, space charge polarization occurs rather slowly and the typical frequency of response is of $\approx 10^2$ Hz. Like dipolar polarization, space-charge polarization is temperature dependent (Cao, 2003; Waser et al., 2005). Figure 2.11 (Cao, 2003) illustrates this mechanism.



Figure 2.11: Space charge polarization mechanism.

The overall polarization of a dielectric system is additive of all the four types of polarization (Cao, 2003). For a dielectric in an alternating field, the total polarizability becomes

$$\alpha_{tot} = \alpha_e + \alpha_{ion} + \alpha_o + \alpha_s \tag{2.12}$$

2.6.4.1 Frequency Dependence of Polarization

When a dielectric is placed in an alternating electric field, the induced dipoles as well as any existing permanent dipoles attempt to maintain alignment with the field. This process requires a finite time that is different for each polarization mechanism. At the relaxation frequency the dipoles are only just able to reorient themselves in tune with the applied field.

At this frequency the dielectric is "lossy" and energy is lost in the form of heat. The dielectric loss is at a maximum when the frequency of the external field coincides with the relaxation frequency of a given polarization mechanism. At frequencies above the relaxation frequency the dipoles are no longer able to keep up with changes in the applied field and the contributing polarization mechanism becomes effectively "frozen" and no longer contributes to the total polarization of the system. In Figure 2.12, a summary of the frequency dependence of the various polarization mechanisms is illustrated for a hypothetical material that exhibits all four of the polarization mechanisms. It shows how polarization P is additive. The peaks occurring at \approx 10 13 and \approx 10 $^{15}\,\text{Hz}$ are due to resonance effects where the external field is alternating at the natural vibrational frequency of the bound ions or electrons, respectively (Carter and Norton, 2007). In normal dielectric materials, the combined value of electronic, ionic and space charge polarization is relatively small and, thus, exerts very small effects of electric polarization on a number of physical properties. In contrast, dipolar polarization may have significant effect on many physical properties (Cao, 2003). The condition is different for ferroelectrics because they are polar crystals and possess reversible spontaneous polarization. The combined effects of the electronic, ionic and space charge polarization are substantial and a significantly large influence occurs in many physical properties such as elastic, optical and thermal behaviour of the material.



Figure 2.12: Frequency dependence of polarization (Carter and Norton, 2007).

2.6.5 Spontaneous Polarization

Spontaneous polarization, P_s , represents a non-zero macroscopic dipole moment existing inside a crystal without any externally applied electric field or stress. The spontaneous polarization is caused by the displacement of the charge centres of the positive and the negative charges in the unit cell (Hirohashi, 2006). In general, P_s is a function of temperature T, and when temperature changes by an amount dT, the change in the spontaneous polarization is given by equation 2.13 below.

$$dP_i = p_i \, dT$$
 where i = 1,2,3 (2.13)

This polarization change is called pyroelectricity (Hirohashi, 2006). When a pyroelectric crystal experiences a homogeneous change in temperature, dipoles orient themselves in one direction and maintain a net polarization. This net polarization vector which is the dipole moment per unit volume is also proportional to the charge per unit volume. These charges appear at the surface of the crystal electrode. As the crystal experiences the homogeneous change in temperature, the charge at the electrode also changes and this change in electrical charge per unit time generates current. Thus, a pyroelectric material produces current as it experiences a change in temperature. This clearly indicates that spontaneous polarization P_s changes has a direct relation to current generation in pyroelectric materials. Therefore, if a change in polarization dP_s is produced by a change in temperature dT in time dt, then the pyroelectric current per unit area of the crystal can be expressed as

$$I_s = \frac{dP_s}{dT}\frac{dT}{dt}$$
(2.14)

where the quantity dP_s/dT is known as the pyroelectric coefficient denoted by p_i and dT/dt is the rate of change of temperature (Hossain and Rashid, 1991).

2.7 Ferroelectrics Hysteresis

Due to the nonlinear dielectric characteristics of ferroelectric materials, hysteresis develops when an electric field is applied along the polar directions of the ferroelectric at a given frequency. A polarization-electric field (P-E) hysteresis loop is the signature of ferroelectricity which appears in the ferroelectric phase. Figure 2.13 is a typical illustration of the features of a ferroelectric hysteresis loop. An ideal hysteresis is generally symmetrical, so the positive and negative coercive fields $\pm E_c$ and the positive and negative remnant polarizations $\pm P_r$ are equal (Damjanovic et al., 2006; Sharma, 2006). At small values of an applied alternating electric field, a linear relationship is developed between polarization P and electric field E. This is because the field is not large enough to switch any domain, thus the sample behaves like a normal dielectric and the portion O to A in Figure 2.13 is obtained according to equation 2.9 (Damjanovic et al., 2006). As the field strength increases, the domains with unfavourable direction of polarization start to switch along directions that are crystallographically as close as possible to the direction of the applied field taking the path A to B. Further increase in the field strength, increases polarization rapidly until all domains are aligned in the direction of the field (Damjanovic et al., 2006; Brewer, 2004). The polarization response in this region is strongly nonlinear and the equation 2.9 is no longer valid (Damjanovic et al., 2006). Once all the domains are aligned the ferroelectric again behaves as a linear dielectric taking the path B to C and the system is said to be saturated with a spontaneous polarization value P_s . At this point, the polarization does not retrace its path when the field is removed. Now when the field strength starts to decrease, some domains switch back to their original orientation due to strain conditions while others remain in the direction of pole making the system take the path B to D. The polarization therefore does not return to zero but attains a finite polarization value at D. This finite polarization in the absence of the electric field is called remnant polarization $+P_r \mu \text{Ccm}^{-2}$ (Ma, 2005) with typical values ranging between 0.001 Cm⁻² and 1 Cm⁻². The arrows indicated at points A, C, D, G and H represent the domain orientation of the system at the various stages of the P-E hysteresis loop cycle. The arrow directions of point A represent a neutral condition where the various domain orientations result in a net zero polarization. The arrow directions of point C and G represent regions of complete polarization saturation during the cycle where almost all the domains are aligned in the direction of the applied field. The arrow directions

of points D and H represents a growing increase in the number of domains aligned in the direction of the applied field. The remnant polarization P_r of the previously poled direction in a ferroelectric sample cannot be removed until the applied field in the opposite direction reaches a certain value. The strength of the field required to reduce the polarization to zero is called the coercive field strength E_c . A further increase in the applied field strength in the opposite direction G. Reversing the field direction once again can complete the hysteresis cycle (Brunahl, 2003).



Figure 2.13: Polarization versus electric field (P-E) hysteresis loop behaviour.

2.8 Domains

Owing to the complex set of elastic and electric boundary conditions at each grain, the ferroelectric grains in polycrystalline materials are always split into many domains (Damjanovic et al., 2006). Ferroelectric domains form to minimize the electrostatic energy due to depolarization fields and the elastic energy associated with spontaneous strain. Domains are separated by domain walls across which the spontaneous polarization P_s



Figure 2.14: Domain evolution in polycrystalline ceramic during the cooling process (Su and Weng, 2006).

is discontinuous. If the angle between the spontaneous polarization orientations of the neighbouring domains is 180° apart, the domain wall is called the 180° domain wall. If the angles are not 180° apart, for example, they are 90° or 71° apart as in a tetragonal and rhombohedral structure respectively, these domains are called 90° or 71° domain wall. The formation of both the 180° and 90° domain wall see Figure 2.15 can minimize the depolarization field by compensating for the surface charge in an unpoled ferroelectric, but only the formation of the 90° domain wall can release the elastic energy stored in the crystal. Moreover, both the 180° and non-180° domain wall motion increases the dielectric properties while only non-180° domain wall motion affects the piezoelectric response (Ma, 2005; Tsurumi et al., 1997; 1998). Phase transformation from a ferroelectric to paraelectric results in a local domain structure with zero net polarization. Figure 2.14 is a depiction of how



Figure 2.15: An illustration of domain walls. (a)180° and (b)90° domain walls.

ferroelectric domains evolve. When a large electric field that is above some coercive field E_c is applied, domains contained within each grain partially align with the external electric field resulting in a net remnant polarization and strain (Oates, 2004). Ferroelectric switching which is the reorientation of the spontaneous polarization leaves majority of the dipoles aligned with the external field. Figure 2.16 is an illustration of ferroelectric switching at the unit cell level. A single crystal that contains no domains is considered as a single-domain or mono-domain state. The single-domain state in single crystal of ferroelectric materials can be achieved by poling.



Figure 2.16: Polarization reorientation in a tetragonal crystal structure at the unit cell.

2.9 Poling of Ferroelectrics

Polycrystalline ferroelectric materials may be brought into a polar state by a process called poling. This process involves applying a strong electric field between 10 KVcm^{-1} and 100 KVcm^{-1} , to the sample for a certain length of time usually at elevated temperatures. An elevated poling temperature decreases crystalline anisotropy and coercive field E_c of the sample. It also increases space charges which decrease domain motion allowing for the development of a single domain. Poling temperatures must however be kept below the transition temperature of the ferroelectric sample. This prevents an increase in the sample's electrical conductivity which consequently increases leakage current and results in sample breakdown during the poling period. The sample being poled must be allowed to cool to room temperature after which the field can be removed. The poling process reorients domains within individual grains along those directions that are permissible by the crystal symmetry and that lie as close as possible to the direction of the field. Poling is only possible in ferroelectrics (Sharma, 2006; Damjanovic et al., 2006). Figure 2.17 shows a ferroelectric ceramic sample before and after poling.



Figure 2.17: An illustration of a ferroelectric ceramic sample before and after poling (Burcsu, 2001).

2.9.1 Ferroelectric Hysteresis Measurement

The simplest method for measuring ferroelectric hysteresis is the Sawyer and Tower method (Kao, 2004). The Sawyer-Tower circuit (Figure 2.18) is simple in concept (Sawyer and Tower, 1930) and it is the original circuit designed for measuring ferroelectric hysteresis. It is essentially a capacitance bridge, relying on the fact that two capacitors in series should have the same charge. One of these capacitors is made with the ferroelectric specimen with capacitance C and the other being a standard linear capacitor with a standard capacitance C_o . This capacitance bridge setup is interfaced with an oscilloscope. The potential across the standard capacitor is plotted on the y-axis and the ac voltage applied to the ferroelectric sample is plotted on the x-axis in the X-Y mode of the oscilloscope. The standard capacitor is chosen to have a large capacitance so that the potential across it is small enough not to affect the potential across the ferroelectric sample. Also, the voltage across C should be sufficiently large to render a saturation in polarization. In the ideal case where the current flowing during this measurement is purely displacive, this measurement will give accurate values of the ferroelectric polarization (Rabe et al., 2007). In order for polarization switching to occur in a ferroelectric, a voltage of an appropriate wave form and amplitude has to be applied.

P-E hysteresis loop measurement circuits do not measure polarization directly. Rather, they measure switched charge Q. By definition, polarization induced in a sample P_{sample} by an electric field is given as

$$P_{sample} = \frac{Q_s}{A} \tag{2.15}$$

Here, Q_s is the charge accumulated on the electrode of the specimen and A is the electrode area. Since the reference capacitor C_o is connected in series to the specimen C, they possess



Figure 2.18: The Sawyer-Tower circuit for the measurement of ferroelectric hysteresis loop. equivalent amount of charges given as $Q_r = Q_s$ where Q_r is the charge on the reference capacitor. The amount of charge on Q_r is given as

$$Q_r = V_o C_o \tag{2.16}$$

where V_o is the voltage across the reference capacitor which is the y-axis value of the hysteresis loop trace on the oscilloscope. The polarization can therefore be obtained from the relation given as

$$P_{sample} = \frac{V_o C_o}{A} \tag{2.17}$$

Consequently, by monitoring the voltage over the reference capacitor, polarization of the specimen can be measured.

The applied electric field E as a function of the voltage drop across the ferroelectric capacitor with capacitance C can also be expressed as

$$E = \frac{V_c}{d} \tag{2.18}$$

where *d* is the thickness of the ferroelectric dielectric layer. By using a ferroelectric capacitor arrangement with a well known geometry, spontaneous polarization P_s , remnant polarization P_r and coercive electric field E_c of the ferroelectric sample can be calculated from the x-axis and y-axis values of the hysteresis loop trace on the oscilloscope.

2.10 Ferroelectric Dielectrics

Ferroelectrics are a special group of dielectrics that exhibit nonlinear dielectric response in the presence of an externally applied electric field. Dielectrics are a class of materials possessing strong bonds between their valence electrons and their positively charged charge centres of their constituent atoms or molecules. This configuration results in the absence of free charge carriers in dielectrics and make dielectric materials good electrical insulators. They are therefore said to be non-metallic materials with high specific resistances and negative temperature coefficient of resistance (Rout, 2006). Dielectrics respond to external electric field by redistributing the charge balance inside the material generating a short range transport of charges and causing small displacements of the positive and negative charges in the opposite directions. This results in the development of induced dipoles in the material. The total polarization of a material depends on the number of dipoles in a unit volume and the polarization direction.

2.10.1 Capacitance and Dielectric Permittivity

Studies of the dielectric properties provide a great deal of information about the suitability of the material for an application. For most applications of ferroelectric materials, κ and

dielectric loss tan δ are important practical parameters.

Ferroelectric electrical measurements are generally made on a sandwich consisting of two electrodes around a dielectric (Valasek, 1921). This sandwich structure (see Figure 2.19) known as a capacitor provides the possibility of applying a field to the ferroelectric (Pazde-Araujo et al., 2001; Harman, 2004). This structure may also consist of metal-ferroelectric-semiconductor or several other possible structural arrangements.



Figure 2.19: The simplest capacitor structure consisting of a dielectric sandwiched between a pair of parallel metallic plates.

The measure of the dielectric medium's ability to hold charges upon the application of voltage across the parallel capacitor plates is called the capacitance. Generally, capacitance C of a capacitor can be expressed as

$$C = \varepsilon \frac{A}{l} \tag{2.19}$$

 ε is the absolute permittivity of the dielectric, *A* is the area of plates and *l* is the separation between the two plates. A more appropriate way of writing equation 2.19 is to replace the absolute permittivity by the product term $\varepsilon_o \varepsilon_r$ where ε_o is the permittivity of free space given as $8 \cdot 8542 \times 10^{-12}$ Fm⁻¹ and ε_r is the relative permittivity usually called dielectric constant (Damjanovic et al., 2006). Capacitance can thus be expressed as

$$C = \varepsilon_o \varepsilon_r \frac{A}{l} \tag{2.20}$$

2.10.2 Dielectric constant

For a given dielectric, the dielectric constant κ or relative permittivity ε_r of that substance is the ratio of the capacitance of a capacitor with that substance as dielectric to the capacitance of the same capacitor with vacuum as dielectric (see equation 2.21).

$$\varepsilon_r = \kappa = \frac{\varepsilon}{\varepsilon_o} \tag{2.21}$$

It is therefore a measure of the amount of electrical charge a given substance can withstand at a given electric field strength. The dielectric constant of any given material varies with temperature and for ferroelectrics, a rapid increase begins near their transition temperature. It also varies as a function of frequency. The dielectric constants of ferroelectrics, such as barium titanate, are substantially high, sometimes many tens of thousands in comparison to normal dielectrics. Due to this property of high dielectric constant, they are mostly used for capacitor fabrication. For an alternating electric field, the dielectric constant can be written as

$$\kappa = \kappa' - i\kappa'' \tag{2.22}$$

where κ' is the real component of the dielectric constant, in phase with the applied field. κ'' is the imaginary component which is 90 ° out of phase with the applied field, caused by either resistive leakage or dielectric absorption.

2.10.3 Dielectric loss

Most dielectrics are generally used in ac applications. They typically experience two kinds of losses comprising conduction loss, representing the flow of actual charge through the dielectric and the other due to movement or rotation of the atoms or molecules. This loss is generally represented by a complex dielectric constant defined in equation 2.22. Contrary to the charging current in an ideal dielectric which leads the applied voltage by $\frac{\pi}{2}$ radians (90°), the total current in the real dielectric is a complex quantity which leads the voltage by an angle (90 – δ)°. The term δ represents the dielectric loss angle. Dielectric loss also known as dissipation factor is defined as

$$\tan \delta = \frac{\kappa''}{\kappa'} \tag{2.23}$$

2.10.3.1 Temperature Dependence of Dielectric Constant

Dielectric constant or permittivity is a very important characteristic of dielectric materials such as ferroelectrics. It is strongly dependent on temperature particularly at the region of the paraelectric-ferroelectric phase transition. The temperature dependence of ε_r can be used to predict the paraelectric-ferroelectric transition temperature of a ferroelectric material. It is also possible to deduce the ferroelectric mechanism of a ferroelectric by observing the temperature dependence of its dielectric constant near the transition temperature. The dielectric constant expresses the behaviour of polarization. Therefore, the dielectric constant value of a ferroelectric is always affected in the vicinity of the phase transition. The variation of the dielectric constant with temperature cannot however be generalized since structural changes accompany ferroelectric phase transitions. Based on equation 2.20, the relation between temperature dependence of capacitance, dielectric constant and thickness can be expressed as

$$\frac{1}{C} \cdot \frac{dC}{dT} = \frac{1}{\kappa} \cdot \frac{d\kappa}{dT} + \frac{l}{A} \frac{dt}{dT} \left(\frac{A}{l}\right)$$
(2.24)

 $\left(\frac{1}{C}, \frac{dC}{dT}\right)$ is defined as thermal coefficient of capacitance (TCC), $\left(\frac{1}{\kappa}, \frac{d\kappa}{dT}\right)$ is defined as the temperature dependence of dielectric constant (TCD) and $\left(\frac{l}{A}\frac{dt}{dT}\left(\frac{A}{l}\right)\right)$ represents dimensional change during thermal expansion (Kao, 2004; Hyun et al., 2005). The relation in equation 2.24 implies that, a change in temperature subsequently changes the capacitance value by changing the capacitor's dimensions and consequently, the value of the dielectric constant (Kao, 2004).

2.11 Current-Voltage Characteristics of Ferroelectrics

Current-voltage behaviour of ferroelectric thin films is important both from a fundamental and application point of view. It can be used to investigate ferroelectric characteristics of a ferroelectrics, such as hysteresis loops and switching current characteristics. The existence of ferroelectricity in ferroelectrics can be verified using switching current behaviour of the thin film (Rabe et al., 2007; Kumar and Nath, 2003; Wang and Chang, 2005). Ferroelectric samples exhibit visible switching peaks at the coercive voltage during the switching process. The εE term in equation 2.11 of section 2.6 contributes to the non-switching process while the spontaneous polarization P_s term contributes to the switching process. The switching current is observed when polarization reversal occurs in ferroelectric capacitors. The applied voltage level determines when the peak point of the switching current appears (Rabe et al., 2007; Kumar and Nath, 2003).

The hysteresis properties of ferroelectrics can be described by capacitance and current at various voltages. Therefore, when an input alternating voltage $V = V_o e^{j\omega t}$ is applied across a ferroelectric thin film capacitor, the slope of the hysteresis loop at a certain voltage V is
essentially the capacitance C at that voltage. For any parallel plate capacitor, it is noted that CV = Q. If the dielectric medium of this capacitor arrangement is linear then

$$C\frac{dV}{dt} = \frac{dQ}{dt} = i_{cap}$$
(2.25)

However, if the medium is also ferroelectric and switches from one state to another during a voltage pulse then

$$C\frac{dV}{dt} + V\frac{dC}{dt} = \frac{dQ}{dt} = i_{total}$$
(2.26)

where $V \frac{dC}{dt} = i_{switch}$ is a consequence of polarization switching which occurs in the ferroelectric phase.

2.12 Geometry and Symmetry Considerations

Generally, all materials undergo small changes in dimension when subjected to an external force. This external force can be an applied electric field, a mechanical stress, or change in temperature. Depending on the material structure, such small changes in dimension may result in a change in electric polarization and subsequently give rise to the occurrence of piezoelectricity, pyroelectricity or ferroelectricity (Kao, 2004). It can be imagined that materials exhibiting these effects must be polar and have an electrical order, implying that they must be crystals or polycrystalline materials composed of crystallites. A crystal or a crystallite must have a definite chemical composition, with the molecules made up of positive and negative ions occupying lattice sites to constitute a crystal structure lattice. The smallest repeating unit of the lattice is called the unit cell and the specific symmetry of the unit cell determines whether the crystal exhibits ferroelectric, piezoelectric, pyroelectric, or

System	Axial lengths and angles
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^{\circ}$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^{\circ}$
Trigonal(Rhombohedral)	$a = b = c, \alpha = \beta = \gamma \neq 90^{\circ}$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^{\circ}$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ}$
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$

Table 2.1: The seven basic crystal system.

electro-optic effects (Kao, 2004). Thus, on the basis of geometry, crystals can be classified into seven Bravais systems illustrated in Table 2.1.

Crystals can also be classified into 230 space groups based on the symmetry elements of translational position and orientation. When translational repetition is ignored, these 230 groups break down into 32 classes, known as the 32 point groups. Point groups are based on orientation only which implies symmetry with respect to a point (Hock, 2004). Any point may be defined by coordinates x, y, and z, with respect to the origin of symmetry. A centrosymmetric crystal is a crystal in which the movement of each point at x, y, z, to a new point at -x, -y, -z, does not cause a recognizable difference. This implies that centrosymmetric crystals are non-polar and thus do not possess a finite polarization or dipole moment. The 32 point groups are broadly grouped into two made up of 11 point groups which are centrosymmetric (possessing a centre of symmetry) and 21 point groups which are non-centrosymmetric (lacking a centre of symmetry) hence possessing the necessary

requirement for piezoelectricity. One of the point groups (432 class) however, though classified as belonging to the noncentrosymmetric class, possesses other combined symmetry elements, thus, rendering no piezoelectricity. So, only 20 classes of noncentrosymmetric crystals exhibit the phenomenon of piezoelectricity (Ma, 2005; Uchino, 2000; Kao, 2004; Webb, 2003) described in section 2.4. 10 of the remaining 20 classes, experiences induced polarization when a mechanical stress is applied while the other 10 classes possess spontaneous polarization. These 10 classes which possess spontaneous polarization are thus permanently polar. Since spontaneous polarization is temperature dependent (Uchino, 2000; Whatmore, 1986) as indicated in section 2.4, these 10 crystal classes therefore exhibit pyroelectric effects in addition to piezoelectric effects (Kao, 2004). There also exists another subgroup within these 10 classes having their spontaneous polarization P_s reversible. Hence, this subgroup can exhibit all three phenomena namely piezoelectricity, pyroelectricity and ferroelectricity. The reversibility of the spontaneous polarization which occurs in this subgroup within these 10 classes characterizes and distinguishes the empirical ferroelectric phenomenon from the other piezoelectric and pyroelectric effects (Kao, 2004). Figure 2.20 is a diagrammatic representation of the crystal symmetry classification and Table 2.2 illustrates crystal classification according to crystal symmetry and polarity. Ferroelectrics are therefore a subset of pyroelectrics which in turn are a subset of piezoelectrics. The converse is however not true (Rabe et al., 2007).



Figure 2.20: Classification of the 32 crystal classes (Roelofs, 2004).

2.13 Classification of Ferroelectrics

Various classification of ferroelectric materials have been proposed to facilitate the treatment of their properties. These classifications are summarized as follows (Neelakanta, 1995):

- 1. Crystal chemical classification which is subdivided into
 - Hydrogen-bonded crystal with examples being Rochelle salt and triglycine sulfate and
 - Double oxides with barium titanate and lead niobate as examples.

Table 2.2: Crystallographic classification according to crystal symmetry and polarity after Uchino (2000).

	Symmetry	Crystal System										
Polarity		Cubic		Hexa- gonal		Tetra- gonal		Rhombo- hedral		Ortho-	Mono-	Tri-
										rhombic	clinic	clinic
Non-Polar	Centre (11)	m3m	<i>m</i> 3	6/mmm	6/m	4/mmm	4/m	3m	3	mmm	2/m	
(22)	Non- centre (21)	432 48m	23	622 ēm2	8	422 42m	ā	32		222		
Polar (Pyro- electric) (10)				8mm	6	4mm	4	3m	3	mm2	2 m	1

- Number of spontaneous polarization allowed directions. This classification is subdivided into
 - Crystals with single axis of spontaneous polarization. Crystals which fall under this classification have only one crystallographic axis along which spontaneous polarization may exist.
 - Crystals with multiple axes of spontaneous polarization. Under this classification, spontaneous polarization may exist in several equivalent crystallographic axes.
- 3. Existence of the lack of centre of symmetry. This classification is employed in the study of the behaviour of ferroelectric crystals. In this classification, ferroelectric crystals such as Rochelle salt and potassium di-hydrogen phosphate are characterized by a noncentrosymmetric non-polar phase whiles crystals such as barium titanate and triglycine phosphate are characterized by a centrosymmetric non-polar phase.
- 4. The nature of phase change occurring at Curie point. Under this classification, there

exist

- the order-disorder and
- the displacive type phase transitions.

Notwithstanding the first three classifications, the fourth classification is the conventional classification of ferroelectrics. Thus, ferroelectric materials are broadly classified into order-disorder and displacive types (Lines and Glass, 1977).

2.13.1 Order-disorder Ferroelectrics

Order-disorder ferroelectrics are typically observed in crystals with hydrogen bonds. The hydrogen atoms in this system jump around some multi potential well configurations above T_c such that there is no net dipole moment. Below T_c the hydrogen atoms jump around some ordered subset of potential wells in such a way that a net dipole moment is produced in the unit cell. Triglycine phosphate and potassium di-hydrogen phosphate are typical examples of ferroelectrics under this category.

2.13.2 Displacive Ferroelectrics

Displacive ferroelectrics are commonly found in ionic materials with typical perovskite structure. The ions attain equilibrium positions, corresponding to a non-polar state above T_c where a net dipole moment is not present. However, below T_c some of the ions shift such that a polar state is introduced in the material. The charge centres of the cations and anions become mutually displaced and thus creates a net dipole moment in the system. Titanates (BaTiO₃, PbTiO₃) and double-oxide ferroelectrics are examples.

2.14 Applications of Ferroelectrics

Primarily, four basic properties of ferroelectric materials are employed for device applications. These include dielectric properties, polarization properties, piezoelectric properties and electro-optic properties (Paz de Araujo et al., 1996). Based on these listed properties, a wide range of commercial and technological applications have been realized from ferroelectrics (Cao, 2003). Ferroelectrics are highly employed in the making of high dielectric constant capacitors based on their dielectric properties. Also, ferroelectrics with high remnant polarization, P_r and low coercive field, E_c , are utilized in the fabrication of non-volatile random access memories (NvRAM) for information storage (Scott and Paz de Araujo, 1989). The possibilities of manufacturing high-density planar dynamic random access memories (DRAM) from ferroelectrics with high dielectric constants, ε_r , has also been proposed by Scott (1998). Piezoelectricity of ferroelectrics has been explored for applications such as displacement transducers, accelerometers, micro-elecro-mechanical systems (MEMS) and actuators which are required for injet printers and for video-recording head positioning. Pyroelectricity of ferroelectrics are also utilized in the fabrication of high-sensitivity, room temperature infrared detectors. Electro-optic activity of ferroelectrics is used in colour-filter devices, displays, image-storage systems and optical switches for integrated optical systems (Polla et al., 1993). Various applications of ferroelectric materials require different combinations of physical properties. However, dielectric constant, remnant polarization P_r and coercive field E_c which are directly related to the reversible spontaneous polarization of ferroelectrics are the key properties required for applications (Cao, 2003).

2.15 Phenomenological Theory of Ferroelectricity

Phenomenological theories treat the macroscopic properties of a material as a continuum. A sufficient number of variables is used to describe a stimulus and its response. Most materials exist in different phases, described by the minima of their thermodynamic potential. Therefore, by means of thermodynamics, relations between the stimulus and the response can be expressed. Such a treatment for ferroelectrics is named after its founders: Landau-Ginzburg-Devonshire (LGD) (Lines and Glass, 1977). Thermodynamic potentials are used as a basis to describe the coupling of different properties in ferroelectrics.

2.15.1 Thermodynamics of Phase Transition

The macroscopic behaviour of ferroelectric systems can be described using classical thermodynamic laws. An understanding of ferroelectric phase transitions and its related effects therefore requires the understanding of the thermodynamic concept of free energy. The basic principle behind thermodynamic treatment is the concept of a minimum free energy for the most stable state. A system with several alternative states will choose the one with the lowest possible free energy. Gibbs free-energy is one such well known function. It includes a pressure-volume pV term and it is given by

$$G = U - TS + pV \tag{2.27}$$

(Kao, 2004). U, S, and T are the internal energy, entropy and temperature of the system respectively.

Since most experiments in solids are carried out at atmospheric pressure, the pV term becomes negligibly small and equation 2.27 becomes

$$G_o = U - TS = A. \tag{2.28}$$

By applying this simple phenomenon based on equation 2.28, a system can have the free energy at the lowest possible value if the internal energy U is as small as possible and the entropy S is as large as possible. The internal energy U in a solid is primarily the potential energy, which is usually a negative quantity. This implies that for a minimum potential energy, all atoms (or ions) must rest at their lattice sites, that is, each atom (or ion) must rest at the bottom of its potential well. This is a well ordered arrangement with very low entropy. But such an arrangement does not lead to a minimum free energy. Not all atoms (or ions) are at the bottom of the potential wells due to the thermal agitation, so the degree of order varies accordingly. At a given temperature T, the value of U and the degree of order S always tend to balance each other in order to reach a stable equilibrium state in which the free energy is the lowest. This is also why all atoms (or ions) in a solid oscillate around their lattice sites. Statistically, entropy is a measure of disorder. The higher the disorder (or the lower the degree of order), the larger is the entropy. Based on thermodynamics, the entropy can be defined as

$$dS = \frac{dQ}{T} = C_p \frac{dT}{T}$$
(2.29)

where dQ is the amount of heat absorbed by the system in a reversible process and C_p is the specific heat at constant pressure (Kao, 2004; Devonshire, 1954).

It is clear from the first law of thermodynamics that an increase in internal energy dU is equal to the sum of the heat put in the system dQ and the work put in the system. Therefore, an external electric field and mechanical stress applied to a solid body causes the internal energy to change according to the relation

$$dU = TdS + Xdh + EdP \tag{2.30}$$

where X and h are the mechanical stress and the strain respectively and E and P are the electric field and the polarization respectively. E and P are vectors, and they have three components in x, y, and z directions. X and h are also vectors and have six components in x, y, and z, as well as shear directions on the plane normal to each of x, y and z, so the energy state of a crystal is specified by the values of nine variables plus the temperature T (Kao, 2004; Devonshire, 1954).

Hence, by including the external work done on a ferroelectric system, thermodynamics can be used to describe the macroscopic behaviour of the ferroelectric system. If the work put in the system is due to external mechanical stresses and electric fields, then the Gibbs function can be written as

$$G = G_o + \sum_i X_i h_i + \sum_j E_j P_j$$
(2.31)

The independent variables in the measurements of normal ferroelectric properties are the temperature *T*, the mechanical stress *X*, and the polarization *P*. Thus, it is convenient to discuss the G function as G(T, X, P). In the absence of mechanical stresses, X = 0 and at a constant *T*, Gibbs function *G* can be simplified to

$$G(T,P) = G_o(T) + \sum_j \frac{P_j^2}{2\varepsilon_{rj}\varepsilon_o}$$
(2.32)

where $G_o(T)$ is the Gibbs function under the unstressed and unpolarized conditions.

2.15.2 Ferroelectric Transition

From equation 2.32 both P_j^2 and ε_{rj} are temperature dependent and their behaviour is anomalous and nonlinear near the transition point. Therefore, the behaviour of the ferroelectric system can be best studied by expanding the energy in powers of the polarization. The Gibbs function for ferroelectrics, formulated on the basis of the form of a power series by Devonshire (1954) is given as

$$G(T, P) = G_o(T) + \frac{1}{2}f_2(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}f_4(P_x^4 + P_y^4 + P_z^4) \frac{1}{2}f_{12}(P_y^2 P_z^2) + P_z^2 P_x^2 + P_x^2 P_y^2) + \frac{1}{6}f_{111}(P_x^6 + P_y^6 + P_z^6) + \frac{1}{2}f_{112}[P_x^2(P_y^2 + P_z^4)] + \frac{1}{6}f_{123}(P_x^2 P_y^2 P_z^2) + \dots$$

$$(2.33)$$

where f_2 , f_4 , f_{12} , f_{111} , f_{112} and f_{123} are temperature-dependent coefficients (Devonshire, 1954; Rabe et al., 2007). The series does not contain terms of odd powers of *P* because crystals in the unpolarized phase have a centre of inversion symmetry. Supposing that the applied poling field is in the *z* direction then the polarization is also along the same *z* direction. By setting $P_y = P_x = 0$ and letting $P_z = P$ for simplicity, equation 2.33 can be simplified to

$$G(T,P) = G_o(T) + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots - EP$$
(2.34)

where a, b and c are new temperature dependent coefficients. For the isothermal case, the electric field E acting on the ferroelectric material, expressed in terms of P, can be obtained by finding the first differential of G with respect to P. That is

$$\frac{dG}{dP} = 0. \tag{2.35}$$

Thus, E is obtained as

$$E = \frac{dG}{dP} = aP + bP^{3} + cP^{5}$$
(2.36)

Now, differentiating equation 2.36 with respect to *P* and setting P = 0 results in the linear dielectric susceptibility χ above the transition.

$$\chi = \frac{dP}{dE} = \frac{1}{a} \tag{2.37}$$

At and near the Curie point, *a* can be approximated with a linear function of temperature and *a* can be written as

$$a = a_o(T - T_o) \tag{2.38}$$

where a_o is taken as a positive constant and T_o may be equal to or close to the Curie transition temperature T_c . Combining equations 2.37 and 2.38, an expression for the dielectric stiffness is obtained as (Nkum, 1989)

$$\frac{1}{\chi} = a_o(T - T_o) \tag{2.39}$$

The dielectric susceptibility χ , captures the Curie-Weiss behaviour observed in most ferroelectrics for $T > T_o$. Substituting equation 2.38 into equation 2.34, leads to the general equation for the free energy expressed as

$$G(T,P) = \frac{1}{2}a_o(T-T_o)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots$$
(2.40)

where a_o and c are both positive in all known ferroelectrics.

The free energy as a function of polarization for a paraelectric $T >> T_o$ and a ferroelectric phase $T << T_o$ is shown in Figure 2.21 and Figure 2.22 respectively. The transformation of

the free energy between these two configurations is determined by the sign of the coefficient b. The sign of b determines the nature of the paraelectric-ferroelectric transition and whether the polarization at $T < T_o$ develops continuously or discontinuously. The simplest case is when all coefficients, except b, are positive and P is continuous at the transition point (Devonshire, 1954; Rabe et al., 2007; Nkum, 1989). In the next two sections, these two configurations that results in either first or second-order transition is discussed.



Figure 2.21: Free energy as a function of temperature for a paraelectric phase (Rabe et al., 2007)



Figure 2.22: Free energy as a function of temperature for a ferroelectric phase (Rabe et al., 2007)

2.15.3 Second-Order (Continuous) Transition

A second-order transition occurs at $T = T_o = T_c$ when b > 0. Under this condition, the free energy evolves continuously as a function of decreasing temperature from P = 0 (Figure 2.21) to a finite minima at $P = \pm P_o$ (Figure 2.22). The spontaneous polarization P_s can be estimated from equation 2.40 by setting E = 0 and retaining the two lowest-order terms since all the coefficients are positive (Devonshire, 1954; Rabe et al., 2007). The results then become

$$P = 0$$
 and

$$P_{o} = \left[\frac{a_{o}}{b}(T_{o} - T)\right]^{\frac{1}{2}}$$
(2.41)

From equation 2.41, it is seen that the spontaneous polarization P_s will increase with decreasing temperature from the point $T = T_o = T_c$. If the dielectric stiffness is determined below the transition ($T < T_o = T_c$) equation 2.42 is obtained. That is,

$$\frac{1}{\chi} = 2a_o(T_o - T)$$
(2.42)

A careful examination of these two expressions in equation 2.42 and 2.39 suggest that $\frac{1}{\chi}$ vanishes at $T = T_o = T_c$ and that consequently the dielectric suseptibility diverges. A skematic description of this transition is shown in Figure 2.23.



Figure 2.23: Characteristic plot of a second-order phase transition. (a) Spontaneous polarization P_s as a function of temperature; (b) The susceptibility χ and its inverse as a function of temperature (Rabe et al., 2007; Kao, 2004); (c) Free energy as a function of the polarization at $T > T_o = T_c$, $T = T_o = T_c$, and $T < T_o = T_c$.

2.15.4 First-Order (Discontinuous) Transition

A first-order transition occurs in the case of b < 0 and equation 2.34 becomes

$$G(T,P) = G_o(T) + \frac{1}{2}aP^2 - \frac{1}{4}|b|P^4 + \frac{1}{6}cP^6 + \dots$$
(2.43)

With the negative quartic coefficient in the equation, it should be clear that even if $T > T_o$ (such that the quadratic coefficient is positive) the free energy may have a subsidiary minimum at nonzero *P*. As *a* is reduced, which corresponds physically to the reduction of

the temperature, this minimum will drop in energy below that of the unpolarized state, and so will be the thermodynamically favoured configuration. The temperature at which this happens is by definition, the Curie temperature T_c , which, however, now exceeds T_o . At any temperature between T_c and T_o the unpolarized phase exists as a local minimum of the free energy. The most important feature of this phase transition is that the order parameter jumps discontinuously to zero at T_c . This type of phase transition is usually called a first-order or discontinuous transition (Rabe et al., 2007; Kao, 2004).

The procedure for finding the spontaneous polarization and the linear dielectric susceptibility is conceptually the same as before, but now one cannot neglect the quartic and sixth-order terms, thus, the minimum $\frac{dG}{dP}$ becomes

$$\frac{dG}{dP} = aP - |b|P^3 + cP^5 = 0.$$
(2.44)

The solution of equation 2.44 yields P = 0 and

$$P = \pm \left\{ \frac{1}{2c} \left[|b| \pm (|b|^2 - 4ca)^{\frac{1}{2}} \right] \right\}^{\frac{1}{2}}$$
(2.45)

For a = 0 where $T = T_c P$ becomes $P = \pm (\frac{|b|}{c})^{\frac{1}{2}}$. This implies that P changes discontinuously from $P = -(\frac{|b|}{c})^{\frac{1}{2}}$ or $P = +(\frac{|b|}{c})^{\frac{1}{2}}$ to P = 0 abruptly at $T = T_c$, and that the transition is of the first-order. Figure 2.24 illustrates the free energy, the spontaneous polarization, the dielectric stiffness and the linear susceptibility as a function of temperature. From this Figure, it can be noted that there exists three energetically degenerate minima at $T = T_o$. Due to this, the system's behaviour at $T = T_c$ will depend on whether it is approaching T_c from lower or higher temperatures. More specifically, the system will be in one of the two finite polarization ($P \neq 0$) minima if it is heated from an initial low temperature $T_i < T_c$, whereas it will be in a paraelectric state (P = 0) if the initial temperature is high ($T_i > T_c$). Indeed, the phenomenon of thermal hysteresis, where the transition temperature depends on whether the sample is heated or cooled, is prevalent in a number of first-order ferroelectrics including barium titanate. It must be emphasized that it is only for $T_o < T_c$ that the ferroelectric minima are thermodynamically favourable (Rabe et al., 2007; Kao, 2004).



Figure 2.24: Characteristic plot of a first-order phase transition. (a) Spontaneous polarization $P_s(T)$ as a function of temperature; (b) Susceptibility χ and its inverse as a function of temperature (c) Free energy as a function of the polarization at $T > T_c$, $T = T_c$, and $T = T_o < T_c$ (Rabe et al., 2007).

In a ferroelectric below T_o there are (at least) two minima of the free energy, corresponding to spontaneous polarizations of different spatial orientations. The barrier between these minima means that a small electric field will not immediately switch the polarization (Rabe et al.,

2007; Kao, 2004).

For ferroelectrics with either continuous or discontinuous transitions, values of the Landau coefficients can be determined by comparing experimental measurements of χ and P_s to the Landau-Devonshire expressions (Rabe et al., 2007; Kao, 2004).

2.15.5 Curie-Weiss Law

Typically, the static dielectric permittivity in the parent phase of a proper ferroelectric material is strongly temperature dependent. Qualitatively, the determined dielectric stiffness (inverse of the linear susceptibility) does not vanish at T_o , but corresponds to the finite jump in both the susceptibility and the spontaneous polarization at the transition. If the poling field is not high, then a first-order approximation can be used by ignoring all terms with the powers of *P* higher than 2 in either equation 2.34 or 2.43 (Kao, 2004). This condition yields the following equation

$$\frac{dG}{dP} = aP = a_o(T - T_o)P \tag{2.46}$$

and *P* for $T > T_c$ can be expressed as

$$P = (\varepsilon_r - 1)\varepsilon_o E = \chi \varepsilon_o E \tag{2.47}$$

For a low-level electric field applied along the prospective ferroelectric axis, the relation 2.48 below is obtained from equation 2.46 and equation 2.47 (Kao, 2004).

$$\chi = \frac{1}{a\varepsilon_o(T - T_o)} = \frac{C}{T - T_o},$$
(2.48)

where $C = (a\varepsilon_o)^{-1}$ is the Curie constant and $T_o(T_o \leq T_c)$ is the Curie-Weiss temperature (Damjanovic et al., 2006). The Curie constant, C, and the Curie-Weiss temperature, T_o , are empirically determined to describe the magnitude of the inverse proportionality of permittivity with temperature. When $T > T_o$ then the thermal movement destroys the ferroelectric state and the material becomes paraelectric. $T_o = T_c$ for a second-order transition and $T_o < T_c$ for a first-order transition as shown in Figure 2.23 and Figure 2.24 respectively. It should be noted that the Curie-Weiss temperature T_o is different from the Curie point T_c . T_o is a formula constant obtained by extrapolation of the linear portion of the Curie-Weiss plot while T_c is the actual temperature where the crystal structure changes at the ferroelectric-paraelectric phase. These two temperatures are not necessarily the same, although they can be (Rabe et al., 2007; Kao, 2004).

2.15.6 Curie Temperature and Curie Point

The actual transition temperature, T_c also called the Curie point and the corresponding value of the spontaneous polarization can be calculated by imposing the condition that the free energy of the polar and the non-polar phases are equal. This leads to

$$\frac{1}{2}a_o(T_c - T_o)P^2 - \frac{1}{4}|b|P^4 + \frac{1}{6}cP^6 = 0.$$
(2.49)

At the same time, the applied field is set equal to zero and this gives

$$E = \frac{dG}{dP} = (T_c - T_o)P - |b|P^3 + cP^5 = 0.$$
 (2.50)

Solving equation 2.49 and 2.50 results in

$$P = \pm \left\{ \frac{3}{4} \left(\frac{|b|}{c} \right) \right\}^{1/2} \tag{2.51}$$

and

$$(T_c - T_o) = \frac{3}{16} \left\{ \frac{|b|^2}{a_o c} \right\}$$
(2.52)

This indicates that the Curie temperature is lower than the actual transition temperature by a factor of $\frac{3}{16} \left\{ \frac{|b|^2}{a_o c} \right\}$.

2.15.7 Thermal Hysteresis

When a ferroelectric crystal is heated through the Curie point, its polarization value changes discontinuously from P = 0 in the ferroelectric phase to P = 0 in the paraelectric non-polar phase. In the first-order transition, the crystal suddenly loses all the energy associated with the polarization at the Curie point, indicating a big change in its latent heat (Kao, 2004). In equation 2.45, for the minimum free-energy condition, there are several distinct values of P for which the free energy G is a minimum. Above T_c there is only one value of P, corresponding to the condition

$$|b|^2 - 4ca_o(T_c - T_o) = 0. (2.53)$$

Thus,

$$T_c = T_o + \frac{|b|^2}{4ca_o}$$
(2.54)

In this case the Curie temperature is lower than the actual transition temperature by

$$\frac{|b|^2}{4ca_o} \tag{2.55}$$

This phenomenon where the transition temperature is always at a slightly lower value when the crystal is cooling from the high temperature than when it is heating from the low temperature is generally referred to as thermal hysteresis (Figure 2.25). This is generally the situation for ferroelectrics with a first-order transition, such as $BaTiO_3$ (Kao, 2004).



Figure 2.25: Order parameters for (a) second and (b) first-order transitions showing thermal hysteresis associated with finite heating and cooling rates (Kao, 2004; IEEE, 2003).

2.16 Optical Constants of Semiconductors

The interaction of a solid with visible and UV radiation causes excitation of valence electrons from filled to empty bands (as in the case of insulators) or within partially filled bands (as in the case of metals). The visible appearance of a solid depends on the degree of absorption and reflectance in the visible region of the electromagnetic spectrum (1.5 to 3.0 eV). Solids with an energy gap in this range will appear coloured (yellow to deeper orange and red, as the bandgap moves down through the visible range of the electromagnetic spectrum). If the bandgap is below 1.5 eV (i.e. infrared), the solid may appear dark in colour or shiny metallic, depending on the reflectivity. If the bandgap is greater than 3 eV (i.e. ultraviolet), no absorption occurs in the visible and a good quality crystal will appear transparent. Furthermore, light may be scattered at defects and crystallite surfaces in the case of a powder sample, which leads to a white appearance. The analysis of optical spectra over a wide range of photon energy has been one of the most productive tools for understanding and developing the theory of electronic structure in crystalline and amorphous solids. Measurement of the optical absorption coefficient α near the fundamental absorption edge is particularly a standard method for the investigation of optically induced electronic transitions in many materials.

When a beam of light (photons) I_o is incident on a material, the intensity of the outgoing light I is expressed by the Lambert-Beer-Bouguer law given as

$$I = I_o exp(-\alpha d) \tag{2.56}$$

where *d* is the thickness of the medium. If this condition for absorption is met, it appears that the optical intensity of the light wave reduces exponentially while traveling through the medium. The measure of how much light this medium absorbs as the light travels through it is expressed by the optical absorption coefficient α . From equation 2.57 it follows that, α is given by

$$\alpha = \frac{2.303}{d} \log\left(\frac{I_o}{I}\right) = 2.303 \frac{A}{d}$$
(2.57)

where A is the optical absorbance and d is the film thickness.

Two types of optical transitions namely direct and indirect, occur at the absorption edge. In a direct transition, the electron's wave vector remains the same (k = 0) and there is no phonon interaction whereas in an indirect transition the cooperation of a phonon is necessary for conserving momentum. With this transition, the electron's wave vector changes $(k \neq 0)$.

The nature of the optical inter-band transition which occurs in the high-absorption region and the value of the energy gap can be determined using the relation derived independently by Tauc et al. (1966) and Mott and Davis (1979) as

$$\alpha(\omega) = \frac{A(\hbar\omega - E_g)^n}{\hbar\omega}$$
(2.58)

where $\alpha(\omega)$ is the absorption coefficient at an angular frequency $\omega = 2\pi v$, \hbar is Planck constant divided by 2π . $n = \frac{1}{2}$ and $\frac{3}{2}$ for allowed direct and forbidden direct transitions and n = 2 and 3 for allowed indirect and forbidden indirect transitions respectively. A is a disorder parameter nearly independent of the photon energy $\hbar \omega$ and E_g is approximately taken as the energy bandgap. Thus the value of the optical bandgap can be obtained by plotting $(\alpha \hbar \omega)^{1/n}$ as a function of photon energy $\hbar \omega$ in the high absorption range followed by extrapolating the linear region of the plot to $(\alpha \hbar \omega)^{1/n} = 0$.

Optical absorbance spectra of amorphous semiconductors generally possess an exponential tail which extends from the absorption edge towards the lower energy regions. This tail region is characterized by an exponential dependence of the absorption coefficient on the photon energy and is called the Urbach edge. The optical absorption coefficient α for the Urbach edge obeys the empirical Urbach rule given as

$$\alpha(E) = \alpha_o exp \frac{\gamma(E - E_g)}{k_B T}$$
(2.59)

where *E* is the energy of the incident radiation, k_B is the Boltzmann constant and α_o is a constant. The factor $\frac{\gamma}{k_B T}$ is a measure of the steepness of the absorption edge and is interpreted as the width of the tail of localized states in the bandgap. The Urbach relation at a particular temperature can be reduced to

$$\alpha(\hbar\omega) = \alpha_o exp\left(\frac{\hbar\omega}{E_u}\right) \tag{2.60}$$

where E_u is the width of the tail of the localized states. The variation of the $\ln(\alpha)$ as a function photon energy $\hbar\omega$, near the absorption edge, illustrates the validity of the Urbach rule (Javed et al., 2008).

2.17 Thin film Deposition

A thin film is defined as a low-dimensional material created by condensing, one-by-one, atomic or molecular or ionic species of matter (Wasa et al., 2004). This characteristic nature of a thin film can be achieved through various deposition techniques.

2.17.1 Deposition Techniques

Various techniques have been developed over the years to deposit thin films. Generally, fabrication techniques produce polycrystalline films which have properties very similar to ceramics than to crystals (Wasa et al., 2004; Burfoot and Taylor, 1979). Thin film fabrication techniques can be divided into two general classes namely physical vapour deposition (PVD) technique and chemical deposition technique. The PVD technique is made up of an atom

source from which atoms are transferred in a continuous and controlled manner under a vacuum atmosphere (> 10^{-5} Torr) to the substrate where the nucleation and growth of the film occur atomistically. This technique is further classified into ion beam sputtering, rf sputtering, electron beam evaporation and laser ablation based on how the atoms or ions are removed from the target. The main disadvantages of the technique are

- the difficulty in controlling the stoichiometry of multicomponent films
- the slow rates of deposition
- the need for high-temperature post deposition crystallization annealing and
- the high cost related with equipment acquisition and maintenance (Vilarinho et al., 2005).

The chemical deposition technique comprises chemical vapor deposition (CVD) and chemical solution deposition (CSD). Chemical vapor deposition relies on reactive gases to transport precursors of the desired materials to the substrate surface. Here they react with other gases or decompose to produce stable products, which are deposited on the substrate. CVD methods are among the most versatile deposition techniques because a wide range of chemical reactants and reactions can be used to deposit a large number of films for a wide application range (Elshabini-Riad and Barlow, 1997). This technique can further be divided into Metal-organic CVD (MOCVD), Plasma-enhanced CVD (PECVD) and Low pressure CVD (LPCVD). CVD is very attractive for industrial manufacturing of functional films. However, the limited availability and toxicity of sources of precursors for functional materials restrict the use of this technology.

Chemical solution deposition (CSD) methods, specially sol-gel, have been increasingly used for the preparation of films of functional materials (Vilarinho et al., 2005). Sol-gel coatings result from spin coating, dip coating or spraying a chemical solution onto a substrate to form a film. This solution is a stable mixture of suspended precursor particles known as sol-gel. Once applied to a substrate, a transition or destabilization of the sol occurs. This is marked by a significant increase in the viscosity of the coating, resulting in the formation of a tacky gel. The gel is hardened to form a film by drying, typically in air. Final film thickness are typically 50 nm to 1 mm (Elshabini-Riad and Barlow, 1997). Other wet processes comprise metal-organic decomposition (MOD), electrochemical reaction and hydrothermal routes which also entail the preparation of the solution, the deposition of the solution onto the substrate by dip or spin coating and the subsequent thermal treatment of the deposited layer to remove the organics and to achieve crystallization and densification of the coatings (Vilarinho et al., 2005). Chemical techniques do not require vacuum ambience, are cheaper and faster, allow for a good stoichiometry control and production of large area defect-free films and often produce films with better properties, although the texture degree of the film is inferior (Vilarinho et al., 2005).

2.17.1.1 Dip Coating Technique

The dip coating technique can be described as a process where a substrate to be coated is immersed in a fluid and then withdrawn with a well defined withdrawal speed under controlled temperature and atmospheric conditions. Coating thickness generally increases with faster withdrawal speeds. The thickness is determined by the balance of forces at the stagnation point on the liquid surface. A faster withdrawal speed pulls more fluid up onto the surface of the substrate before it has time to flow back down into the solution. Figure 2.26 illustrates the several technical stages involved in the film formation process. The underlying chemical and physical processes involved in this formation processes may



Figure 2.26: Stages involved in dip coating deposition technique after Aegerter and Mennig (2004).

however overlap (Aegerter and Mennig, 2004). Starting with the immersion of the substrate, a coherent liquid film is entrained on withdrawal of the substrate from the coating fluid which then consolidates by drying. Normally, to obtain a final coating material, a further curing or sintering step is necessary. The thickness is primarily affected by fluid viscosity, fluid density and surface tension. If the withdrawal speed is chosen such that the sheer rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation given as

$$h = c \times \frac{(\eta \nu)^{2/3}}{\gamma^{1/6} \rho g^{1/2}}$$
(2.61)

where *h* is the coating thickness, *c* is a constant (0.944 for Newtonian fluid), η denotes the liquid viscosity, *v* the withdrawal speed, γ the surface tension of the liquid against air, ρ the liquid density and *g* as gravity. The exponent in the withdrawal speed *v* strongly depends on the chemical properties of the coating liquid and it ranges between 0.5 to 0.7.

CHAPTER 3

EXPERIMENTAL DETAILS

This chapter discusses the materials and experimental procedures used in obtaining the results of this work.

The KNO₃ ferroelectric material used in this work was obtained from BDH Chemicals Limited, Poole, England. The purity of the salt as quoted by the manufacturer was 99.5 %. Pre-cleaned superfrost microscope slides from MENZEL-GLASER, Germany, a 99.9 % purity nickel (Ni) metal sheet from BDH Chemicals Limited, a 99.9 % purity tantalum (Ta) metal sheet from BDH Chemicals Limited and an austenitic stainless steel (SS) were used as substrate electrode materials. The electrical measurements of this work were carried out on the KNO₃ thin film samples deposited on elemental metal substrates (Ni, SS and Ta) and the film samples prepared on glass slides were used for the optical measurement. The selected microscope slides were chosen to be of high transparency in the UV/visible range required for the optical measurements.

3.1 Sample Preparation

The choice of a particular preparation technique for a particular ferroelectric material may vary from one to another depending on the application and on the nature of characterization being undertaken. In this study, the technique employed for the preparation of the samples used in this work was adapted from Nolta and Schubring (1962), El-Kabbany et al. (1988) and Dawber et al. (2003) in their work on KNO_3 .

3.1.1 Substrate Electrode Preparation

Two sets of rectangular shaped metal strips of widths 1.0 cm and 0.4 cm were cut from the nickel, stainless steel and tantalum metals while one set of rectangular shaped glass strip of width 1.0 cm was cut from the microscope glass slides (Figure 3.1a). The 1.0 cm width metal strips and 1.0 cm width glass strips served as the substrates used for the deposition of the KNO₃ thin films while the 0.4 cm width metal strips were further processed into top electrodes by making a $0.4 \text{ cm} \times 0.4 \text{ cm}$ square bend at one end of the strip as shown in Figure 3.1b. Each of these square ends served as a parallel electrode plate to its corresponding deposited substrate electrode.





(a) Sample cutout metal and glass strips. (i) 0.4 cm width metal strip (ii) 1.0 cm width metal strip (iii) 1.0 cm width glass strip.

(b) A sample 0.4×0.4 cm square bend made at one end of a 0.4 cm width metal strip.



These cutout glass and metal strips were cleaned with detergent, distilled water and 99.5 % assay analytical grade acetone and dried in a furnace at 300 °C for a period of 30 minutes. This cleaning process ensured the complete removal of grease from the substrate and enhanced the adhesion of the deposited film to the substrate. Figure 3.2 is a picture of some prepared substrates ready for deposition.



Figure 3.2: Prepared metal and glass substrates ready for deposition.

3.1.2 Thin Film Preparation

A customized dip coating unit based on the dip coating deposition technique (page 73) was successfully designed (Figure 3.3) and constructed to prepare the KNO_3 thin films used in this work. The relatively low melting point of KNO_3 ensured an easy conversion of its powdered into the molten form. In this form, it was easier to dip and coat a substrate and as well preserve the ferroelectric property of the material since the presence of moisture degrades the ferroelectric property of KNO_3 (Nolta and Schubring, 1962).

3.1.2.1 Design and Construction of a Dip Coating Unit

As mentioned above, a home-built dip coating unit was used to deposit the KNO₃ thin film samples used in this work. As can be seen in the design shown in Figure 3.3, the unit (Figure 3.4) is made up of a temperature-controlled oven compartment which was used in converting the KNO₃ salt into molten form. The oven compartment is a two container system separated by a glass wool lag. The two container oven system and the lag were employed in the design to slow down the cooling rate of the unit. Other components of the unit include a spindle motor for the purposes of substrate withdrawal, a thermocouple thermometer for temperature monitoring, a rack to mount substrates and a crucible stand to carry the crucible that holds the molten salt. The rack component of the unit has an incision at one end with a screw lock system. This configuration was used to hold attached substrates in place.



Figure 3.3: The structural design of the home-built dip coating unit.



Figure 3.4: A picture of the home-built dip coating unit.

The substrate holder was designed such that it is able to accommodate two substrates per deposition. The substrate withdrawal system is made up of the spindle motor with a gear attached to its shaft and to the rack to which the substrates are attached. The gear attached to the spindle motor engaged the rack whenever the motor was switched on, consequently lifting the rack, and thus raising the substrates through the molten salt.

3.1.2.2 KNO₃ Thin Film Deposition

The (KNO_3) thin films were deposited with the above described home-built dip coating unit as follows. The crucible was filled with KNO_3 salt and placed in the unit's crucible stand. The various substrates were in turn attached to the substrate holder and positioned few millimeters above the crucible. The oven compartment of the unit was then switched

on and regulated to heat within the range of 480 °C and 520 °C. The unit was then allowed to remain within this temperature range for about an hour by which time all the salt was now molten. The attached substrates were then dipped into the molten salt for a duration of 30 minutes to ensure that they attained the same temperature as that of the molten salt. This was also done to aid film-substrate adhesion. After the 30-minute duration had elapsed, the motor was switched on allowing the attached substrate to be slowly raised through the molten KNO₃ fluid to few millimeters above it. At this point, still within the unit, the deposited film was allowed to solidify and cool to room temperature. The samples used in the optical measurements were deposited at about 480 °C and 520 °C to investigate the effect of deposition temperature on the optical bandgap of KNO₃ thin film while all the samples used for the electrical measurements were deposited at about 500 °C.

3.1.3 Ferroelectric KNO₃ Capacitor Arrangement

From subsection 2.10.1 (page 43), it is noted that ferroelectric electrical measurements are generally carried out using a capacitor. This arrangement makes it possible to apply a polarizing field to the ferroelectric via the capacitor plates where these plates serve as electrical contacts.

Ferroelectric KNO₃ capacitors used for the electrical measurements of this work were obtained as follows. The $0.4 \text{ cm} \times 0.4 \text{ cm}$ square bend end (see Figure 3.1b) of the 0.4 cm width metal strip was clamped to its corresponding 1.0 cm width metal strip (see Figure 3.5c) on which the KNO₃ thin film was deposited with the aid of a jaw vice as shown in Figure 3.5c. By this parallel plate capacitor arrangement, the deposited KNO₃ thin film was sandwiched and thus, served as a ferroelectric dielectric. The resulting capacitors obtained from this

metal/ KNO_3 /metal capacitor structure were Ni/ KNO_3 /Ni for the nickel top electrode and substrate electrode, SS/ KNO_3 /SS for the stainless steel top electrode and substrate electrode and Ta/ KNO_3 /Ta for the tantalum top electrode and substrate electrode.

Figure 3.5 shows the components of this capacitor structure and as well illustrates the capacitor fabrication process. Samples of the 0.4 cm width metal strips having the 0.4 cm \times 0.4 cm square bend at one end are shown in Figure 3.5a while the pair of matching metal strips are shown in Figure 3.5b. Figure 3.5c shows the jaw vice having a capacitor sample clamped in its jaws and made ready for experimental runs. Figure 3.5d is a sample taken out of the jaw vice after measurement runs.



(a) The $0.4 \text{ cm} \times 0.4 \text{ cm}$ square bends made at the ends of the 0.4 cm width metal strips.



(c) A deposited substrate electrode plate and a corresponding matching top electrode plate clamped in a jaw vice to form a capacitor.



(b) The matching metal strip pairs which form the parallel plate for the ferroelectric KNO_3 capacitor.



(d) A clamped capacitor sample.

Figure 3.5: An illustration of the components which formed the KNO_3 capacitor used in this work.

3.2 Measurements

3.2.1 Film Thickness Determination

The Leica DM2500 M light microscope was used in determining the thicknesses of the various films formed on both the glass and metal substrates. The reflectance mode of the microscope was used. The upper and lower film surfaces were focused to obtain the focusing difference between these two film surfaces. The film thickness was given by the stage height difference occurring as a result of the focusing difference between the upper and lower film surfaces of the film layer (LeicaMicrosystems, 2007).

3.2.2 P-V Hysteresis Loop Measurement

The Sawyer-Tower method discussed in subsection 2.9.1 (page 41) was used to obtain electrical polarization loops of the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta capacitor samples. A home-built Sawyer-Tower unit (Figure 3.7) based on the Sawyer-Tower circuit shown in Figure 2.18 (page 42) was constructed and used for this purpose. A 0.1μ F standard capacitor was used as the reference capacitor (C_o) in this home-built Sawyer-Tower unit used for this measurement. Figure 3.6 shows the block diagram illustration of the setup used.

Since spontaneous polarization (P_s) is temperature dependent (see section 2.6.5), the sample temperature had to be varied to enable charges that developed on the electrodes due to spontaneous polarization to be measured. A changing temperature environment created by an oven (see Figure 3.8), was therefore used to trigger the pyroelectric phenomenon in the ferroelectric dielectric layers of the capacitor samples used.


Figure 3.6: Block diagram for P-V loop measurements.



Figure 3.7: Home-built Sawyer-Tower method P-V loop measurement unit.

The measurement setup was connected as shown in Figure 2.18. A DF1643 function generator was used to supply a 20 V (50 Hz) sine wave signal while a 20 MHz BK Precision (model 2522A) oscilloscope was connected to the X and Y outputs of the Sawyer-Tower unit to display P-V loops exhibited by the samples. A Sony Cyber shot 10.1 mega pixels camera was then used to record the observed P-V loops. Measurements were made as samples were taken through both heating and cooling cycles between the temperature of 30 °C and 180 °C. The sample temperature was monitored at every 0.1 °C change in temperature with

a PHYWE CIE 305 thermocouple thermometer.



Figure 3.8: The Sawyer-Tower method P-V loop tracer experimental setup used in this work.

The voltages corresponding to the x-axis and y-axis of the exhibited P-V hysteresis loops were then obtained from the hysteresis displays. The obtained y-axis voltage was in two forms. The values obtained from the extrapolation of the linear portion BC (see Figure 2.13 page 37) to the y-axis gave one set of voltages while the point where the hysteresis loop cut the y-axis gave the other set of voltages. These two sets of y-axis voltages were used to calculate the spontaneous polarization P_s and remnant polarization P_r respectively using equation 2.17 (see page 42). The x-axis voltage values obtained from the hysteresis loop were also used to calculate the coercive field E_c across the sample using equation 2.18 (see page 42).

3.2.3 Current density-Voltage Measurement

From subsection 2.11, it is noted that the hysteresis phenomenon of a ferroelectric at a certain voltage V can be described by the capacitance C and the switching current i_{switch} as expressed in the relation $V\frac{dC}{dt} = i_{switch}$. Hence, from a current density-voltage measurement, the existence of a ferroelectric phase can be verified. The P-V hysteresis loop exhibited by the samples were thus verified by current density-voltage measurements.

The circuit in Figure 3.9 comprising a standard resistor of resistance $20 \text{ K}\Omega$ in series with KNO_3 capacitor was used to display switching peaks on an oscilloscope (BK Precision model 2522A) during the ferroelectric phase of the sample. The $20 \text{ K}\Omega$ resistor was used to drop most of the voltage across the ferroelectric sample. A sine wave signal supplied by a DF1643 function generator was used for this measurement. The sample temperature was varied with an oven and was monitored with a PHYWE CIE 305 thermocouple thermometer. Two opposite sharp peaks were expected to appear as polarization switching occurred during the ferroelectric phase of the samples.



Figure 3.9: Current density-voltage (J-V) measurement circuit.

3.2.4 Dielectric Constant Temperature Dependence Measurement

The temperature dependence of the dielectric constant of each of the ferroelectric capacitors was investigated using the setup shown in Figure 3.10. This aspect of the work was used to determine the paraelectric-ferroelectric phase transition temperature as well as characteristics. The anomaly which characterizes the dielectric property of a ferroelectric in the vicinity of the paraelectric-ferroelectric transition formed the basis of this characterization. Since the dielectric constant anomaly of a ferroelectric in the vicinity of a transition is of a large magnitude, it can be deduced from equation 2.24 (page 46) that the changes in capacitance during the paraelectric-ferroelectric phase transition is significantly caused by changes in the dielectric constant of the dielectric layer and not because of dimensional changes of the capacitor.



Figure 3.10: An experimental setup for measuring the variation of capacitance with temperature

At every 0.1 °C drop in temperature, the capacitance of the sample was measured with a capacitance meter (precision gold PG012 DMM). The temperature monitoring was done with a PHYWE CIE 305 thermocouple thermometer. From these measured capacitances, C, the relative permittivity (dielectric constant) ε_r of sample at every 0.1 °C temperature change was calculated using equation 2.20 (page 44). The area component *A* of this relation was the area of the plates of the capacitor. Since the effective plate area forming the capacitor was 0.4 cm x 0.4 cm (see Figure 3.1b page 77), an area of 0.16 cm² was used. The parameter *l* of the capacitance relation was the thickness of the KNO₃ dielectric layer of the capacitor sample.

The obtained dielectric constants were then plotted as a function of temperature (T) to observe their dependence on temperature. For ferroelectrics, inverse dielectric constants, $1/\varepsilon_r$ can replace dielectric susceptibility. Therefore, $1/\varepsilon_r$ of the samples were also calculated from ε_r . $1/\varepsilon_r$ was then plotted as a function of temperature to observe the Curie-Weiss behaviour (see subsection 2.15.5 page 65) of the sample. From these plots, the Curie point T_c and the Curie-Weiss temperatures (T_o) were obtained. For a second-order transition, the linear portions of both wings of the $1/\varepsilon_r$ (T) are extrapolated to the abscissa to obtain the Curie point, T_c . $T_c=T_o$ for a second order transition while $T_c \neq T_o$ for a first-order transition. It was therefore possible to determine the order of the ferroelectric transition by obtaining T_c and T_o from $1/\varepsilon_r$ temperature dependence plots.

3.2.5 Optical Absorbance Spectrum Determination

The optical bandgap, E_g and the Urbach energy, E_u of the KNO₃ thin film used in this work were evaluated from absorbance spectrum obtained from a UV-Vis absorption spectroscopy. Measurements were carried out at room temperature using a SHIMADZU UVmini-1240 UV/VIS scanning spectrophotometer (Figure 3.11) in the spectral range of 300 nm to 900 nm. The optical absorption method which is the most direct and simplest method of determining optical constants was used to determine the optical band gap of the thin film.



KNO thin film deposited on a glass substrate

(a) A picture of the SHIMADZU UVmini-1240 UV/VIS spectrophotometer containing a sample.



KNO thin film deposited on a glass substrate

(b) The sample chamber of the spectrophotometer shown in (a) enlarged to display a sample positioned for measurement

Figure 3.11: A SHIMADZU UVmini-1240 UV/VIS spectrophotometer for optical absorbance measurements.

Figure 3.11 is a picture of a SHIMADZU UVmini-1240 UV/VIS scanning spectrophotometer with a sample positioned for measurements. Each sample scan was preceded with a baseline scan of an empty glass slide which eliminated the effect of the substrate in the spectrum. The absorption coefficient (α) below and near the edge of the absorbance spectrum of each film was determined at selected wavelengths using equation 2.57 in section 2.16. From equation 2.58 (see section 2.16 page 68), it can be observed that α is related to the photon energy ($\hbar\omega$) as

$$\alpha \hbar \omega = A (\hbar \omega - E_g)^n \tag{3.1}$$

Using equation 3.1 (see page 90), the optical bandgap for the direct transition (where n = 1/2) for each sample was obtained by plotting $(\alpha\hbar\omega)^2$ as a function of photon energy $(\hbar\omega)$ and extrapolating the linear portion of the plot to the $(\hbar\omega)$ axis. Similarly the optical bandgap for the indirect transition (for the case where n = 2) was obtained by plotting $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy $(\hbar\omega)$ and extrapolating the linear portion of the plot to the $(\hbar\omega)$ axis.

The Urbach energies of the samples were also investigated using equation 2.60 (page 71). From this relation, Urbach plots of $\ln(\alpha)$ as a function photon energy $\hbar\omega$ was obtained. The Urbach energies E_u of each sample was then calculated by taking the reciprocal of the slope of the linear portion in the lower photon energy region of the Urbach curves.

CHAPTER 4

EXPERIMENTAL RESULTS

The home-built dip coating unit described in subsection 3.1.2.1 was successfully used to deposit KNO₃ thin films on both metal and glass substrates as can be seen in Figure 4.1. Thicknesses ranging from $1.0\,\mu\text{m}$ to $2.0\,\mu\text{m}$ were obtained with the metal substrate while thicknesses ranging from $1.5\,\mu\text{m}$ to $2.0\,\mu\text{m}$ were obtained with the glass substrates. For the films deposited on the metal substrates, KNO₃/Ni, KNO₃/SS and KNO₃/Ta samples were obtained after deposition. The deposited films were observed to be transparent in nature. The thin films with thicknesses of $1.0\,\mu\text{m}$, $1.3\,\mu\text{m}$ and $1.5\,\mu\text{m}$ were chosen and used for the electrical characterizations carried out in this research while the optical property measurements were carried out with $1.5\,\mu\text{m}$ KNO₃/Ta samples together with their corresponding top electrodes were used to form Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta parallel plate capacitors with KNO₃ acting as dielectric. (see subsection 3.1.3).



Figure 4.1: KNO₃ thin films deposited on metal and glass substrates

4.1 Effect of Substrate Electrodes on Phase Transition Characteristics of the KNO₃ Thin Films

The fabricated ferroelectric capacitors of KNO₃ were used in investigating the dielectric properties of KNO₃ thin films deposited on Ni, SS and Ta substrates respectively. The capacitance of each of the KNO₃ capacitors was recorded as the sample cooled from about 180 °C to room temperature. Since capacitance C of a dielectric is related to its dielectric constant ε_r , the temperature dependence of ε_r could be derived from the capacitance-temperature measurements. The dielectric constant, ε_r , at every 0.1°C change in temperature was calculated. The temperature dependence of the dielectric constant ε_r and the inverse dielectric constant $\frac{1}{\varepsilon_r}$ were then plotted for each sample. The anomalous behaviour of ε_r above T_c (T > T_c) which closely follows the Curie-Weiss relation was then investigated with the plot of $\frac{1}{\varepsilon_r}$ as a function of temperature T. In this section, the temperature dependence of the dielectric layer between the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta are presented.

4.1.1 Ni/KNO₃/Ni Dielectric Film Layers

The temperature dependence of ε_r of the dielectric layer of the Ni/KNO₃/Ni capacitor sample was investigated to determine the influence of the Ni substrate electrode on KNO₃ ferroelectric dielectric layer. The plots in Figures 4.2a, 4.2b and 4.2c depict the temperature dependence characteristics of ε_r and $\frac{1}{\varepsilon_r}$ for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ dielectric layers respectively.

As the $1.0\,\mu\text{m}$ KNO₃ dielectric layer cooled from the paraelectric phase to the ferroelectric

phase, a sharp rise and fall was observed in the ε_r in the vicinity of 120.4 °C (see Figure 4.2a). In a similar fashion, as the 1.3 μ m and 1.5 μ m KNO₃ dielectric layers cooled though the paraelectric-ferroelectric phase, a sharp rise and fall occurred in the ε_r in the temperature region of 121.0 °C and 123.5 °C respectively (see Figures 4.2b and 4.2c).

The linear portion of both wings of the $\frac{1}{\varepsilon_r}$ (T) plot in the region of the anomaly (i.e., T>T_c and T<T_c) were extrapolated to the temperature (T) axis to obtain the Curie points (T_c) of the dielectric layers. A T_c of 120.5 °C, 121.0 °C and 123.4 °C were respectively obtained for the 1.0 μ m, 1.3 μ m and 1.5 μ m ferroelectric KNO₃ dielectric layer of the Ni/KNO₃/Ni capacitor samples.

Since ε_r attains a simple form above T_c , $\frac{1}{\varepsilon_r}$ varied linearly with temperature and thus obeys the Curie-Weiss relation. An extrapolation of the linear region of the Curie-Weiss plot above T_c to the temperature axis also yielded the Curie-Weiss temperature (T_o) of 120.5 °C, 121.0 °C and 123.4 °C respectively for the 1.0 μ m, 1.3 μ m and 1.5 μ m ferroelectric KNO₃ dielectric layer. These T_c 's and T_o 's can also be seen in Table 4.1. T_o was observed to be equal to T_c for each Ni/KNO₃/Ni sample.



(a) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.0 μ m KNO₃ thin films deposited on nickel substrate.

(b) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.3 μ m KNO₃ thin films deposited on nickel substrate.



(c) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.5 μ m KNO₃ thin films deposited on nickel substrate.

Figure 4.2: Temperature dependence of the dielectric constant ε_r and inverse dielectric constant $1/\varepsilon_r$ for the Ni/KNO₃/Ni thin films studied in this work.

4.1.2 SS/KNO₃/SS Dielectric Film Layers

During the cooling experimental run of the SS/KNO₃/SS capacitor to investigate the effect of SS substrate electrode on the KNO₃ ferroelectric dielectric layer, the characteristic plots shown in Figures 4.3a, 4.3b and 4.3c were obtained for the $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m KNO₃ dielectric layers respectively.

At the point of transition from the paraelectric phase to the ferroelectric phase, a sharp rise and fall was observed in the dielectric constants of these samples. For the 1 μ m SS/KNO₃/SS sample, this anomaly occurred in the vicinity of 148.2 °C (see Figure 4.3a) while that of the 1.3 μ m SS/KNO₃/SS and 1.5 μ m SS/KNO₃/SS samples occurred in the vicinity of 141.7 °C (see Figure 4.3b) and 145.2 °C (see Figure 4.3c) respectively.

To determine the exact transition temperature, the linear portion of the two wings which occurred as a result of the anomaly were extrapolated to the temperature (T) axis. A Curie point T_c of 148.0 °C, 141.5 °C and 145.0 °C were respectively obtained for the 1.0 μ m, 1.3 μ m and 1.5 μ m ferroelectric KNO₃ dielectric layer of the SS/KNO₃/SS capacitor samples.

For each sample, the anomalous behaviour of ε_r above T_c closely followed the Curie-Weiss relation. By extrapolating the linear portion of the $\frac{1}{\varepsilon_r}$ (T) plot of the paraelectric region to the temperature (T) axis , the Curie-Weiss temperature T_o for each sample was obtained. The T_o 's obtained were observed to be the same as the T_c 's for each sample as can be seen in Table 4.1





(a) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.0 μ m KNO₃ thin films deposited on stainless steel substrate.

(b) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.3 μ m KNO₃ thin films deposited on stainless steel substrate.



(c) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.5 μ m KNO₃ thin films deposited on stainless steel substrate.

Figure 4.3: Temperature dependence of the dielectric constant ε_r and inverse dielectric constant $1/\varepsilon_r$ for the SS/KNO₃/SS thin films studied in this work.

4.1.3 Ta/KNO₃/Ta Dielectric Film Layers

The ε_r of the cooling KNO₃ dielectric layer of the Ta/KNO₃/Ta capacitor was investigated to determine the influence of the Ta substrate electrode on KNO₃ ferroelectric dielectric layer. The temperature dependence plots of ε_r and $\frac{1}{\varepsilon_r}$ shown in Figures 4.4a, 4.4b and 4.4c were obtained for the 1.0 μ m, 1.3 μ m and 1.5 μ m Ta/KNO₃/Ta capacitor samples respectively.

On approaching the vicinity of the paraelectric-ferroelectric transition, the ε_r of each sample exhibited an anomaly as was observed in the Ni/KNO₃/Ni and SS/KNO₃/SS samples. For the 1.0 μ m capacitor sample, this occurred in the temperature region of 120.0 °C (see Figure 4.4a). In the case of the 1.3 μ m and 1.5 μ m Ta/KNO₃/Ta capacitor samples, it occurred in the vicinity of 124.0 °C (see Figure 4.4b) and 121.4 °C (see Figure 4.4c) respectively.

The Curie point and Curie-Weiss temperatures of the samples were then obtained by employing the technique used for the previous two samples. The obtained Curie points (T_c) were 120.0 °C, 124.0 °C and 121.6 °C respectively for the $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m ferroelectric KNO₃ dielectric layer of the Ta/KNO₃/Ta capacitor samples. The obtained T_c 's were the same as the Curie-Weiss temperatures (T_o) as is shown in Table 4.1.





(a) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.0 μ m KNO₃ thin films deposited on tantalum substrate.

Temperature, T (oC)

(b) Temperature dependence of ε_r and $1/\varepsilon_r$ for the 1.3 μ m KNO₃ thin films deposited on tantalum substrate.



thin films deposited on tantalum substrate.

Figure 4.4: Temperature dependence of the dielectric constant ε_r and inverse dielectric constant $1/\varepsilon_r$ for the Ta/KNO₃/Ta thin films studied in this work.

From Table 4.1, the Curie points obtained for the Ni/KNO₃/Ni and Ta/KNO₃/Ta samples agreed with the reported inherent Curie point of KNO₃ irrespective of the dielectric layer thickness. The SS/KNO₃/SS samples however deviated from this temperature, recording Curie points of about 20.0 °C higher than the inherent Curie point. Also, as already stated above, for each specific sample, T_c and T_o were the same.

Table 4.1: Curie points (T_c) and Curie temperatures (T_o) of the ferroelectric KNO₃ dielectric layer of the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta Samples.

Sample	Dielectric Thicknesses (µm)	Τ _c (°C)	Т ₀ (°С)
Ni/KNO ₃ /Ni	1.0	120.5	120.5
	1.3	121.0	121.0
	1.5	123.4	123.4
SS/KNO ₃ /SS	1.0	148.0	148.0
	1.3	141.5	141.5
	1.5	145.0	145.0
Ta/KNO ₃ /Ta	1.0	120.0	120.0
	1.3	124.0	124.0
	1.5	121.6	121.6

4.2 Effect of Substrate Electrodes on Polarization

During the polarization-electric field and current density-voltage measurements to investigate the P-V and J-V characteristics of the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta thin film samples, the P-V loops exhibited hysteresis while the J-V curves developed switching peaks within certain temperatures. In this section, these characteristic P-V hysteresis loops and J-V curves for the $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m thin film samples are presented.

4.2.1 Characteristic P-V Loop and J-V Curve of the Cooling $1.0 \,\mu m$ Ni/KNO₃/Ni Thin Film Sample

Figures 4.5, 4.6 and Figure A.1a in Appendix A show the characteristic P-V loops and J-V curves exhibited by the cooling $1.0 \,\mu$ m Ni/KNO₃/Ni thin film sample. In the vicinity of 120.5 °C, hysteresis phenomenon and polarization switching peaks respectively appeared in the P-V loop and J-V curve. This condition denoted the onset of the ferroelectric phase in this sample. The switching peaks seen in the J-V curve as well as the hysteresis nature of the P-V loop became very well defined with decreasing temperature until the maximum possible polarization was attained between the temperatures of 106.0 °C and 101.5 °C. Under the condition of maximum possible attainable polarization, the observed P-V hysteresis loop remained unchanged and a P_s of $4.12 \,\mu$ C/cm² was attained. The ferroelectric phase of this sample which existed up to about 40.0 °C, was generally characterized by a square shaped P-V hysteresis loop. The P-V loop no longer exhibited the hysteresis phenomenon when the sample cooled below 40.0 °C.



Figure 4.5: 111.6 °C and 106.0-101.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu$ m KNO₃ thin film prepared on Ni.



Figure 4.6: 85.5 °C and 40.3 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on Ni.

4.2.2 Characteristic P-V Loop and J-V Curve of the Heating $1.0 \,\mu m$ Ni/KNO₃/Ni Thin Film Sample

In Figures 4.7, 4.8 and Figure A.4a in Appendix A, the characteristic P-V loop and J-V curve exhibited by the $1.0 \,\mu$ m Ni/KNO₃/Ni thin film sample during heating are shown. As the sample temperature increased to about 77.5 °C, hysteresis and switching peaks respectively occurred in the P-V loop and J-V curve of the sample. The P-V hysteresis loop increasingly became well defined as temperature increased until about 160.0 °C when it began to diminish. A square shaped hysteresis loop generally characterized the temperatures between about 95.0 °C and 150.0 °C. This sample attained it maximum possible polarization between 152.6 °C and 154.5 °C and within this temperature range, the P-V hysteresis loop remained unchanged. This condition resulted in a P_s of $3.15 \,\mu$ C/cm². The hysteresis nature of the P-V loop and the switching peaks which occurred in the J-V curve were no longer evident above 170.0 °C.



Figure 4.7: 77.5 °C and 100.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on Ni.



Figure 4.8: 116.0-118.0 °C and 152.6-154.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu m$ KNO₃ thin film prepared on Ni.

4.2.3 Temperature Dependence of P_s , P_r and E_c for the 1.0 μ m Ni/KNO₃/Ni Thin Film Sample

The P_s , P_r and E_c associated with the P-V hysteresis loops obtained via electric field cooling and electric field heating of the $1.0 \,\mu$ m Ni/KNO₃/Ni thin film were transformed into temperature dependence plots to show how these hysteresis loop parameters varied with temperature.

The P_s and P_r values as well as the E_c of this 1.0 μ m Ni/KNO₃/Ni thin film sample was observed to change with temperature variations. As the sample cooled, P_s and P_r increased while E_c decreased until a certain temperature range where the maximum possible attainable polarization occurred. Within this temperature range, all three parameters remained constant though the sample temperature continued to decrease. As the temperature decreased further beyond the temperature region where maximum polarization was attained, P_s and P_r now decreased while E_c increased. The increase seen in E_c continued until the temperature when P_s and P_r decreased gradually. At this point E_c attained a constant value again and afterwards decreased. From the plots in Figure 4.10a, it can be observed that the 1.0 μ m Ni/KNO₃/Ni film attained a P_r value of 2.88 μ C/cm² at maximum possible polarization which occurred between about 106.0 °C and 105.5 °C on cooling. The sample experienced an initial E_c of about 8.0 MV/cm at the onset of ferroelectricity but this decreased with decreasing temperature until a value of 5.0 MV/cm was attained at maximum polarization. The sample then experienced a rise in E_c, reaching a maximum between the temperatures of 65.0 °C and 50.0 °C.

During heating, P_s , P_r and E_c slowly increased until about 140.0 °C when an abrupt rise was seen in P_s and P_r while E_c dropped sharply. After maximum possible polarization had been attained, P_s and P_r decreased sharply while E_c increased and then maintained a constant value as P_s and P_r gradually approached zero. This observation is depicted in the plots shown in Figure 4.10b. A P_r of $2.74 \,\mu C/cm^2$ and a coercive field of about 4.9 MV/cm was observed across the sample at maximum polarization between 152.0 °C and 155.0 °C during the heating run. E_c however increased to about 6.5 MV/cm as temperature continued to increased until the hysteresis phenomenon of the P-V loop was no longer evident.



(a) Variation of P_s, P_r and E_c with cooling sample temperature for the 1.0 μ m KNO₃ thin film deposited on nickel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.0 μ m KNO₃ thin film deposited on nickel substrate.

Figure 4.9: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with sample temperature for the 1.0 μ m Ni/KNO₃/Ni thin film.

4.2.4 Characteristic P-V Loop and J-V Curve of the Cooling $1.3 \mu m$ Ni/KNO₃/Ni Thin Film Sample

The characteristic P-V loop and J-V curve exhibited during the cooling of the $1.3 \mu m$ Ni/KNO₃/Ni thin film sample can be seen in Figures 4.10, 4.11 and Figure A.1b in Appendix A. At about 121.0 °C, hysteresis phenomenon was seen in the P-V loop and polarization switching peaks appeared in the J-V curve of the sample. This occurrences marked the onset of the ferroelectric phase of this sample. As the sample temperature continued to decrease, the hysteresis phenomenon of the P-V loop became increasingly evident. Between the temperatures of 110.9 °C and 106.5 °C, the maximum possible attainable polarization was reached and the P-V hysteresis loop remained constant in its shape. This condition resulted in a P_s of 2.44 μ C/cm². The ferroelectric hysteresis exhibited during the ferroelectric phase of this 1.3 μ m Ni/KNO₃/Ni thin film sample was also generally square-like in shape as was the case of the 1.0 μ m Ni/KNO₃/Ni thin film sample. The P-V hysteresis phenomenon and the J-V switching peaks were no longer evident as the sample cooled below 45 °C.



Figure 4.10: 118.5 °C and 110.9-106.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu$ m KNO₃ thin film prepared on Ni.



Figure 4.11: 75.0 °C and 45.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ni.

4.2.5 Characteristic P-V Loop and J-V Curve of the Heating $1.3 \mu m$ Ni/KNO₃/Ni Thin Film Sample

During the heating run for the $1.3 \,\mu$ m Ni/KNO₃/Ni thin film sample, the characteristic P-V loop and J-V curve shown in Figures 4.12, 4.13 and Figure A.4b in Appendix A were exhibited. Hysteresis phenomenon was seen in the P-V loop and switching peaks appeared in the J-V curve of the sample as the sample temperature increased to about 77.0 °C. As temperature increased further to about 100.0 °C, the P-V hysteresis loop became very well defined exhibiting a square shaped hysteresis loop. Between the temperatures of about 148.5 °C and 149.2 °C during heating, the condition of maximum polarization was reached. Under this condition, the P-V hysteresis loop remained unchanged in shape and a P_s of $1.76 \,\mu$ C/cm² was attained. As temperature increasing beyond 160.0 °C, the observed P-V hysteresis and the J-V switching peaks diminished and was no longer evident.



Figure 4.12: 76.5 °C and 100.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ni during heating.



Figure 4.13: 148.5-149.2 °C and 160.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ni during heating.

4.2.6 Temperature Dependence of P_s , P_r and E_c for the 1.3 μ m Ni/KNO₃/Ni Thin Film Sample

The P_s , P_r and E_c parameters associated with the P-V hysteresis loop exhibited by the 1.3 μ m Ni/KNO₃/Ni thin film sample were transformed into temperature dependence plots to investigate their temperature dependence characteristics.

At the onset of the ferroelectric phase during cooling, P_s and P_r initially increased gradually within a very short temperature range and then abruptly after. E_c which was stable at the onset also dropped sharply as P_s and P_r began to exhibit a sharp rise. This trend of a sharp rise and a sharp drop continued until the maximum possible polarization was attained. All three parameters now remained constant within this temperature range where saturation was attained. Here after, P_s and P_r now dropped sharply but a rather gradual increase was seen in E_c . As P_s and P_r decreased towards the lower temperature end of the ferroelectric phase, E_c now began to rise faster until it attained a constant value at lower P_s and P_r values. Hereafter E_c now dropped sharply as the very low temperature end of the phase was approaching. From the plots in Figures 4.15a, it can be seen that the 1.3 μ m Ni/KNO₃/Ni thin film sample produced a P_r value of 2.15 μ C/cm² at maximum polarization which occurred between about 111.0 °C and 106.5 °C on cooling. A coercive field of 5.8 MV/cm was also observed across the sample at about 115.0 °C under this same condition of maximum polarization.

The plots in Figure 4.15b, depict the temperature dependence characteristics of the P_s , P_r and E_c of the 1.3 μ m Ni/KNO₃/Ni thin film sample during heating. P_s and P_r slowly increased gradually as the sample temperature increased until about 140.0 °C where an abrupt rise was observed. After the maximum possible polarization was attained, P_s and P_r now exhibited a fast downward trend while a rise was observed in E_c . As P_s and P_r diminished at high

temperatures, E_c maintained a constant value. A P_r of $1.54 \,\mu\text{C/cm}^2$ and E_c of 6.9 MV/cm was observed across the sample under the condition of maximum polarization which occurred at about 148.5 °C on heating.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.3 μ m KNO₃ thin film deposited on nickel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.3 μ m KNO₃ thin film deposited on nickel substrate.

Figure 4.14: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with sample temperature for 1.3 μ m Ni/KNO₃/Ni thin film.

4.2.7 Characteristic P-V Loop and J-V Curve of the Cooling $1.5 \mu m$ Ni/KNO₃/Ni Thin Film Sample

The characteristic P-V loops and J-V curves exhibited by the 1.5 μ m Ni/KNO₃/Ni thin film sample during the cooling run are shown in Figures 4.15, 4.16 and Figure A.1c in Appendix A. The appearance of polarization switching peaks in the J-V curve and the development of a hysteresis by the P-V loop at about 123.4 °C marked the onset of the ferroelectric phase of this sample. As the sample cooled through the temperatures between 112.4 °C and 110.5 °C, the P-V hysteresis loop no longer changed in shape. This occurrence marked the condition of the maximum possible attainable polarization and this consequently resulted in a P_s of 2.65 μ C/cm². As temperature continued to decrease, the switching peaks which appeared in J-V curve and the hysteresis phenomenon of the P-V loop diminished until it was no longer evident below 40.0 °C. A square shaped P-V hysteresis loop generally characterized the ferroelectric phase of this sample.



Figure 4.15: 120.0 °C and 112.4-110.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu$ m KNO₃ thin film prepared on Ni.



Figure 4.16: 65.5 °C and 51.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ni.

4.2.8 Characteristic P-V Loop and J-V Curve of the Heating $1.5 \,\mu m$ Ni/KNO₃/Ni Thin Film Sample

Figures 4.17, 4.18 and Figure A.4c in Appendix A show the characteristic P-V loop and J-V curve exhibited by the $1.5 \mu m$ Ni/KNO₃/Ni thin film sample during the heating run. Hysteresis phenomenon and polarization switching peaks were respectively observed in the P-V loop and J-V curve of this sample at about 70.0 °C as the sample temperature increased. At 100.0 °C, a square shaped hysteresis loop was attained and this generally characterized the rest of observed P-V loop. An unchanging P-V hysteresis loop was observed between the temperatures of 155.0 °C and 157.0 °C. This condition which signified the maximum possible polarization resulted in a P_s of 2.63 μ C/cm². As temperature increased above 157.0 °C, the hysteresis phenomenon of the P-V curve and the switching peaks which appeared in the J-V curve gradually diminished. Above 167.0 °C, these characteristics of the P-V loop and the J-V curve was no longer present.



Figure 4.17: 70.0 °C and 113.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ni during heating.



Figure 4.18: 155.0-157.0 °C and 167.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the $1.5 \,\mu$ m KNO₃ thin film prepared on Ni during heating.

4.2.9 Temperature Dependence of P_s , P_r and E_c for the 1.5 μ m Ni/KNO₃/Ni Thin Film Sample

The temperature dependence of P_s , P_r and E_c for the 1.5 μ m Ni/KNO₃/Ni thin film sample were investigated as was done in the case of the 1.0 μ m and 1.3 μ m samples by transforming the recorded P-V hysteresis loop obtained via the electric field heating and electric field cooling of this sample into P_s , P_r and E_c versus temperature (T) plots.

The trend observed in these P_s , P_r and E_c versus temperature (T) plots were similar to the trend exhibited by the 1.0 μ m and 1.3 μ m Ni/KNO₃/Ni samples. As this sample cooled, P_s and P_r were seen to increase while E_c which was initially constant decreased. This observed temperature dependence trend continued until maximum possible polarization was reached. Under this condition of polarization temperature, P_s , P_r and E_c maintained a constant value. As temperature decreased below the region of saturation, E_c increased slowly while P_s and P_r sharply dropped. This trend continued until the very low temperature end of the phase when E_c began to decrease again as P_s and P_r diminished. From the plots shown in Figures 4.20a, it can be seen that maximum possible polarization occurred between about 112.4 °C and 110.5 °C resulting in a P_r of 2.34 μ C/cm². The E_c seen across this sample also decreased from about 7.0 MV/cm to about 5.0 MV/cm within the temperature range where maximum possible polarization occurred.

The plots in Figure 4.20b, depict the temperature dependence of P_s , P_r and E_c for the 1.5 μ m Ni/KNO₃/Ni thin film sample. P_s , P_r increased slowly as temperature increased while a rather

fast increase of E_c occurred as the sample temperature rose during heating. In the vicinity of 140.0 °C, an abrupt rise was observed in P_s and P_r but E_c dropped sharply. This trend continued until the maximum possible polarization was attained between about 155.0 °C and 157.0 °C. Within this temperature range, P_s , P_r and E_c remained constant. After this region of maximum possible polarization, P_s and P_r decreased sharply while E_c increased sharply. E_c attained a constant value shortly after and remained at this value till P_s and P_r diminished. A P_r of 2.26 μ C/cm² and a coercive field of 5.2 MV/cm was seen across the sample at maximum polarization.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.5 μ m KNO₃ thin film deposited on nickel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.5 μ m KNO₃ thin film deposited on nickel substrate.

Figure 4.19: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with sample temperature for $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m Ni/KNO₃/Ni thin films.
4.2.10 Comparison between P_s and P_r for the Ni/KNO₃/Ni Thin Film Samples obtained During Heating and Cooling

The plots in the Figures 4.21a, 4.21b, 4.21c and 4.21d show the comparison between the P_s and P_r attained by the 1.0 μ m, 1.3 μ m and 1.5 μ m Ni/KNO₃/Ni thin film samples during both the heating and cooling experimental run. Generally, a similar trend was exhibited by all samples irrespective of the thickness of the KNO₃ film layer.

The P_s and P_r attained by the 1.0 μ m Ni/KNO₃/Ni sample were higher under both cooling and heating conditions compared to those attained by the 1.3 μ m and 1.5 μ m Ni/KNO₃/Ni samples as can be seen from the plots. The P_s and P_r values attained by both the 1.3 μ m and the 1.5 μ m Ni/KNO₃/Ni samples were closely related during the cooling. This however changed during heating. Relatively higher values of P_s and P_r were attained by the 1.5 μ m sample under the heating condition in comparison to that attained by the 1.3 μ m sample.



(a) Variation of P_s with cooling sample temperature for the $1.0\,\mu\text{m}$, $1.3\,\mu\text{m}$ and $1.5\,\mu\text{m}$ KNO₃ thin films deposited on nickel substrate.



(c) Variation of P_s with heating sample temperature for the $1.0\,\mu\text{m}$, $1.3\,\mu\text{m}$ and $1.5\,\mu\text{m}$ KNO₃ thin films deposited on nickel substrate.



(b) Variation of P_r with cooling sample temperature for the $1.0\,\mu\text{m}$, $1.3\,\mu\text{m}$ and $1.5\,\mu\text{m}$ KNO₃ thin films deposited on nickel substrate.



(d) Variation of P_r with heating sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on

Figure 4.20: Relation between P_s and P_r for the 1.0 μ m, 1.3 μ m and 1.5 μ m Ni/KNO₃/Ni thin films sample as the KNO₃ sample temperature changed during the heating-cooling cycle.

nickel substrate.

4.2.11 Characteristic P-V Loop and J-V Curve of the Cooling $1.0 \,\mu$ m SS/KNO₃/SS Thin Film Sample

The characteristic P-V loop and J-V curve shown in Figures 4.21, 4.22 and Figure A.2a in Appendix A were recorded during the ferroelectric phase of the $1.0 \mu m$ SS/KNO₃/SS thin film sample. At about 148.0 °C, the phenomenon of hysteresis was seen in the P-V loop of the sample while polarization switching peaks also occurred in J-V curve observed at this temperature. These occurrences marked the onset of the ferroelectric phase of this sample. The P-V hysteresis loop increasingly became well developed with decreasing temperature until the temperatures between 126.0 °C and 120.5 °C when it remained constant. Under this condition, a P_s of 3.38μ C/cm² was attained. Below 120.5 °C, P_s consistently reduced as the sample temperature decreased. However, this 1.0μ m thin film sample still exhibited a well defined P-V hysteresis loop even at room temperature. Consequently, the J-V curves recorded at room temperature also showed polarization switching peaks. A square shaped P-V hysteresis loop generally characterized the ferroelectric phase of this sample.



Figure 4.21: 148.0 °C and 126.0-120.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu$ m KNO₃ thin film prepared on SS.



Figure 4.22: 50.0 °C and 30.1 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on SS.

4.2.12 Characteristic P-V Loop and J-V Curve of the Heating $1.0 \,\mu$ m SS/KNO₃/SS Thin Film Sample

The $1.0\,\mu\text{m}$ SS/KNO₃/SS thin film sample on heating from room temperature exhibited the characteristic P-V hysteresis loop and J-V curve shown in Figures 4.23, 4.24 and Figure A.5a in Appendix A. As the sample temperature increased from room temperature, the hysteresis phenomenon of its P-V loop and as well as the switching peaks which existed in its J-V curve increasingly became prominent. The observed P-V hysteresis loop increasingly became well defined as the sample temperature increased until between 167.0 °C and 171.0 °C when it remained constant notwithstanding the increasing sample temperature. This stability in the P-V hysteresis loop was due to the condition of maximum attainable polarization. At this point, a P_s of $3.75\,\mu\text{C/cm}^2$ was attained. A square shaped hysteresis loop also generally characterized the P-V loop exhibited by this sample during heating.



Figure 4.23: 30.1 °C and 107.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on SS.



Figure 4.24: 167.0-171.0 °C and 181.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu m$ KNO₃ thin film prepared on SS.

4.2.13 Temperature Dependence of P_s , P_r and E_c for the 1.0 μ m SS/KNO₃/SS Thin Film Sample

The P-V hysteresis loop parameters associated with the P-V hysteresis loop obtained via electric field cooling and electric field heating of the $1.0 \,\mu\text{m}$ SS/KNO₃/SS thin film sample were transformed into temperature dependence plots to investigate the temperature dependence characteristics of P_s, P_r and E_c.

As this sample cooled through its ferroelectric phase, P_s and P_r increased sharply and became saturated within some short temperature range. P_s and P_r now drop to some value a little below its original saturation value and then began to increase again until another region of maximum polarization was attained. Hereafter, P_s and P_r drop sharply. E_c which was initially constant sharply dropped within the temperature region where P_s and P_r attained saturation. E_c began to increase after the region of maximum polarization. This increase in E_c continued as P_s and P_r decreased with decreasing temperature. From the plots shown in Figure 4.26a, The maximum possible attainable polarization occurred between about 126.0 °C and 120.5 °C as the sample cooled. A P_r of 2.88 μ C/cm² was attained under this condition. The E_c observed across the sample under this condition of saturation was 6.0 MV/cm. This value however increased to about 8.5 MV/cm as the sample lost its ferroelectricity.

On heating, the P_s , P_r and E_c of this 1.0 μ m SS/KNO₃/SS thin film sample slowly increased as temperature increased until an abrupt rise in P_s and P_r occurred. An initially constant E_c also exhibited a sharp rise and then maintained a constant value until about 120.0 °C when it sharply dropped. P_s , P_r and E_c maintained a constant value within the temperature range when maximum polarization occurred. Beyond the temperature of saturation, P_s , P_r now decreased sharply while E_c increased until it attained a constant value. From the temperature dependence plot of P_r shown in Figure 4.26b, it can be seen that this $1.0 \,\mu m$ SS/KNO₃/SS thin film sample attained a P_r of $3.30 \,\mu C/cm^2$ at maximum polarization which occurred between about 167.0 °C and 171.0 °C. It can also be noted that the coercive field E_c which developed across the sample at saturation was 5.0 MV/cm. This however increased to about 6.0 MV/cm as temperature increased until the ferroelectric phase was lost.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.0 μ m KNO₃ thin film deposited on stainless steel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.0 μ m KNO₃ thin film deposited on stainless steel substrate.

Figure 4.25: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with changing sample temperature for $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m SS/KNO₃/SS thin films.

4.2.14 Characteristic P-V Loop and J-V Curve of the Cooling $1.3 \mu m$ SS/KNO₃/SS Thin Film Sample

Figures 4.26, 4.27 and Figure A.2b in Appendix A show the characteristic P-V loop and J-V curve exhibited by the $1.3 \mu m$ SS/KNO₃/SS thin film sample during the cooling experimental run. The phenomenon of hysteresis which was observed in the vicinity of 141.5 °C in the P-V loop coupled with the appearance of switching peaks in the J-V curve at this same temperature marked the onset of the ferroelectric phase of this sample. As temperature decreased, the P-V hysteresis loop increasingly became well defined and on reaching the temperatures between 115.8 °C and 114.0 °C no changes were observed in its shape. This occurrence was due to the sample attaining its maximum possible polarization. This condition resulted in a P_s of 2.90 μ C/cm². Below 35.0 °C, the P-V loop was no longer hysteric and switching peaks disappeared from the J-V curve of this sample. A square shaped



Figure 4.26: 141.5 °C and 116.2-113.9 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu$ m KNO₃ thin film prepared on SS.



Figure 4.27: 50.0 °C and 39.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on SS.

4.2.15 Characteristic P-V Loop and J-V Curve of the Heating $1.3 \,\mu m$ SS/KNO₃/SS Thin Film Sample

In Figures 4.28, 4.29 and Figure A.5b in Appendix A, the characteristic P-V loop and J-V curve exhibited by the $1.3 \,\mu\text{m}$ SS/KNO₃/SS thin film sample as its temperature increased from room temperature to about 180.0 °C are shown. On heating to about 77.0 °C, the sample's P-V loop showed the phenomenon of hysteresis. Polarization switching peaks also appeared in the J-V curve recorded at this temperature. The P-V hysteresis loop became square shaped at about 85.5 °C and generally remained in this form until the loop was no longer hysteric at high temperatures. Between the temperatures of 146.5 °C and 150.0 °C, the P-V hysteresis loop remained constant in shape. This was due to the condition of maximum polarization and this resulted in a P_s of $3.15 \,\mu\text{C/cm}^2$. Above 165.0 °C, the P-V loop no longer exhibited the phenomenon of hysteresis and switching peaks disappeared from the J-V curve.



Figure 4.28: 77.5 °C and 100.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on SS.



Figure 4.29: 146.5-150.0 °C and 162.9 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.3 \,\mu m$ KNO₃ thin film prepared on SS.

4.2.16 Temperature Dependence of P_s , P_r and E_c for the 1.3 μ m SS/KNO₃/SS Thin Film Sample

The P-V hysteresis loop parameters associated with the P-V hysteresis loops obtained via electric field cooling and electric field heating for the $1.3 \,\mu m$ SS/KNO₃/SS thin film were transformed into temperature dependence plots to show how P_s, P_r and E_c of this sample varied with temperature.

The P_s , P_r and E_c of the SS/KNO₃/SS samples varied with temperature as the sample cooled through the ferroelectric phase. P_s and P_r increased while E_c decreased as the sample temperature decreased. This trend exhibited by P_s , P_r and E_c continued until the maximum possible polarization was attained. Under this condition of maximum polarization, all these three parameters remained constant. As temperature cooled beyond this region, P_s and P_r sharply decreased while E_c sharply increased. As P_s and P_r approached zero close to the lower temperature end of the ferroelectric phase, E_c attained a constant value and then began to drop sharply. From the plots in Figure 4.31a, it can be seen that this 1.3 μ m SS/KNO₃/SS sample attained maximum polarization between about 116.0 °C and 114.0 °C on cooling. A resulting P_r of 2.69 μ C/cm² and a coercive field of 5.4 MV/cm were observed under this condition of saturation. The coercive field however increased as temperature decreased until it reached about 8.0 MV/cm.

On heating, the P_s , P_r and E_c of this $1.3 \,\mu m$ SS/KNO₃/SS sample exhibited temperature dependence. A gradual increase was initial observed in P_s and P_r as temperature increasing until a sharp rise occurred at about 80.0 °C. Under this same condition, a sharp drop occurred in E_c . As the sample temperature continued to increase, P_s and P_r reached saturation and then began to fall while E_c now increased until it attained a constant value on approaching

the higher temperature region. From the plots in Figure 4.31b, the maximum possible polarization attained by this sample resulted in a P_r of $2.80 \,\mu\text{C/cm}^2$ between about 146.0 °C and 150.0 °C. A coercive field of 5.0 MV/cm developed across the sample at maximum polarization; however, this increased to about 7.0 MV/cm as P_s and P_r decreased until the ferroelectric phase was lost.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.3 μ m KNO₃ thin film deposited on stainless steel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.3 μ m KNO₃ thin film deposited on stainless steel substrate.

Figure 4.30: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with changing sample temperature for 1.0 μ m, 1.3 μ m and 1.5 μ m SS/KNO₃/SS thin films.

4.2.17 Characteristic P-V Loop and J-V Curve of the Cooling $1.5 \,\mu$ m SS/KNO₃/SS Thin Film Sample

The characteristic P-V loop and J-V curve exhibited by the $1.5 \,\mu\text{m}$ SS/KNO₃/SS thin film sample during cooling are displayed in Figures 4.31, 4.32 and Figure A.2c in Appendix A. The ferroelectric phase of this sample appeared at 145.0 °C and was marked by the phenomenon the hysteresis which occurred in the P-V loop and the appearance of switching peaks in the J-V curve recorded at that temperature. As temperature decreased, the P-V hysteresis loop increasingly became well formed until the temperatures between 120.0 °C and 116.0 °C when no changes occurred in its shape. This occurrence signified the maximum possible attainable polarization. Under this condition, a P_s of 2.90 μ C/cm² was attained. A square shaped hysteresis loop generally characterized this sample's ferroelectric phase until the hysteresis nature of the P-V loop and the J-V switching peaks disappeared below 35.0 °C.



Figure 4.31: 145.0 °C and 120.0-116.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu$ m KNO₃ thin film prepared on SS.



Figure 4.32: 50.0 °C and 37.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on SS.

4.2.18 Characteristic P-V Loop and J-V Curve of the Heating $1.5 \,\mu$ m SS/KNO₃/SS Thin Film Sample

The $1.5 \,\mu\text{m}$ SS/KNO₃/SS thin film sample exhibited the P-V loop and J-V curve shown in Figures 4.33, 4.34 and Figure A.5c Appendix A during heating. As the sample temperature increased to about 80.5 °C, the hysteresis phenomenon was observed in the sample's P-V loop while the J-V curve recorded at this temperature showed polarization switching peaks. The P-V hysteresis loop observed during the heating of this sample became square shaped and generally characterized the shape of the P-V loop as temperature increased. Polarization increased as temperature increased until the temperatures between 154.2 °C and 158.9 °C

when the P-V hysteresis loop remained unchanged. This was the condition of maximum possible attainable polarization and a resulting P_s of $2.88 \,\mu\text{C/cm}^2$ was attained. Above 172.0 °C, the hysteresis phenomenon of the P-V loop ans well as the switching peaks observed in the J-V curve disappeared.



Figure 4.33: 80.5 °C and 130.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on SS.



Figure 4.34: 154.2-158.9 °C and 172.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.5 \,\mu m$ KNO₃ thin film prepared on SS.

4.2.19 Temperature Dependence of P_s , P_r and E_c for the 1.5 μ m SS/KNO₃/SS Thin Film Sample

The temperature dependence of P_s , P_r and E_c for the 1.5 μ m SS/KNO₃/SS were investigate by transforming the hysteresis loop parameters associated with the P-V hysteresis loop obtained via electric field cooling and electric field heating into temperature dependence plots.

The P_s , P_r and E_c of the 1.5 μ m SS/KNO₃/SS thin film sample varied with temperature as the sample cooled through the ferroelectric phase. P_s and P_r exhibited an increase as temperature decreased while E_c decreased as temperature decreased. As P_s and P_r attained saturation, E_c

now maintained a constant value. As temperature decreased below the region of maximum polarization, P_s and P_r now decreased sharply while E_c increased slowly. As P_s and P_r diminished close to the lower temperature end of the ferroelectric phase, E_c again became constant and then dropped sharply. From the plots shown in Figure 4.36a it can be noted that this sample yielded a P_r of 2.90 μ C/cm² at saturation which occurred between about 120.0 °C and 116.0 °C. The sample experienced a 5.3 MV/cm coercive field (E_c) across it under this condition of saturation but this increased to about 8.0 MV/cm as P_s and P_r decreased.

During heating the P_s , P_r and E_c of this 1.5 μ m SS/KNO₃/SS thin film sample exhibited the temperature dependence characteristics shown in the plots of Figure 4.36b. P_s and P_r increased gradually with increasing temperature until the vicinity of 80.0 °C when a sharp rise was observed until maximum possible polarization was attained. The E_c across the sample similarly increasing slowly with increasing temperature until it attained a constant value. Close to the temperature region where P_s and P_r exhibited an abrupt rise, E_c dropped sharply. Between 152.0 °C and 159.0 °C where P_s and P_r attained saturation, E_c remained constant. Beyond this temperature region, E_c now increased again as P_s and P_r decreased sharply. From the plots (see Figure 4.36b), a P_r of 2.60 μ C/cm² and a coercive field of 4.8 MV/cm occurred at maximum polarization. E_c however increased to about 6.4 MV/cm as temperature increased.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.5 μ m KNO₃ thin film deposited on stainless steel substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.5 μ m KNO₃ thin film deposited on stainless steel substrate.

Figure 4.35: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with changing sample temperature for $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m SS/KNO₃/SS thin films.

4.2.20 Comparison between P_s and P_r for the SS/KNO₃/SS Thin Film Samples obtained During Heating and Cooling

From the plot shown in Figures 4.37a, 4.37b, 4.37c and 4.37d, it can be noted that the P_s and P_r of the 1.0 μ m SS/KNO₃/SS sample extended over a wider temperature range compared to that of the 1.3 μ m and 1.5 μ m SS/KNO₃/SS samples. For this 1.0 μ m sample, the ferroelectric phase existed even at room temperature while the phase was no longer evident close to room temperature for the 1.3 μ m and 1.5 μ m samples. P_s and P_r was also seen to increase with decreasing film thickness. Thus, the 1.0 μ m SS/KNO₃/SS sample attained the highest P_s and P_r values followed by the 1.3 μ m sample and the 1.5 μ m SS/KNO₃/SS sample successively.



(a) Variation of P_s with cooling sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on stainless steel substrate.



(c) Variation of P_s with heating sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on stainless steel substrate.



Temperature, T (°C)

(b) Variation of P_r with cooling sample temperature for the $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m KNO₃ thin films deposited on stainless steel substrate.



(d) Variation of P_r with heating sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on stainless steel substrate.

Figure 4.36: Spontaneous polarization P_s (a), remnant polarization P_r (b) and coercive field E_c (b) variation with changing sample temperature for $1.0 \,\mu\text{m}$, $1.3 \,\mu\text{m}$ and $1.5 \,\mu\text{m}$ SS/KNO₃/SS thin films sample.

4.2.21 Characteristic P-V Loop and J-V Curve of the Cooling $1.0 \,\mu$ m Ta/KNO₃/Ta Thin Film Sample

The $1.0 \,\mu\text{m}$ Ta/KNO₃/Ta thin film sample exhibited the P-V loop and J-V curve shown in Figures 4.37, 4.38 and Figure A.3a in Appendix A as it cooled through the ferroelectric phase. Polarization switching peaks appeared in the J-V curve at about 120.0 °C and this marked the onset of the ferroelectric phase of this sample. As temperature continued to decrease, the P-V loop became hysteric in shape though this P-V hysteresis loop remained unsaturated all through the ferroelectric phase. On reaching the temperature range between 116.5 °C and 115.0 °C on cooling, the P-V hysteresis loop maintained a constant loop shape and this marked the condition of maximum attainable polarization. A P_s of 2.38 μ C/cm² was attained under this condition of maximum polarization.



Figure 4.37: 120.0 °C and 116.5-115.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu$ m KNO₃ thin film prepared on Ta.



Figure 4.38: 61.0 °C and 57.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.22 Characteristic P-V Loop and J-V Curve of the Heating $1.0 \,\mu$ m Ta/KNO₃/Ta Thin Film Sample

Figures 4.39, 4.40 and Figure A.6a in Appendix A show the characteristic P-V loop and J-V curve exhibited by the $1.0 \,\mu$ m Ta/KNO₃/Ta thin film sample during heating. On heating to about 88.0 °C, polarization switching peaks appeared in the J-V curve of this sample. As the temperature of the sample continued to increase, the hysteresis phenomenon was seen in the sample's P-V loop. Though this P-V hysteresis loop did not become well defined and remained unsaturated as temperature increased, its hysteresis nature was quite evident. The maximum possible attainable polarization occurred briefly at about 160.0 °C and this resulted in a P_s of $1.88 \,\mu$ C/cm².



Figure 4.39: 88.5 °C and 120.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.



Figure 4.40: 160.0 °C and 167.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.0 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.23 Temperature Dependence of P_s , P_r and E_c for the 1.0 μ m Ta/KNO₃/Ta Thin Film Sample

The P_s, P_r and E_c associated with the P-V hysteresis loop exhibited during the electric field heating and electric field cooling of the $1.0 \,\mu$ m Ta/KNO₃/Ta thin film sample were plotted against temperature to study their temperature dependence as follows: As this sample cooled through the ferroelectric phase, its P_s, P_r and E_c followed the trend depicted by the plots shown in Figure 4.42a. From the onset of the ferroelectric phase, P_s and P_r increased as temperature decreased while E_c decreased as temperature decreased. On reaching the condition of maximum possible polarization, all three parameters then remained constant. Below the temperature region where maximum polarization occurred, P_s and P_r now decreased while E_c increased. A P_r of $1.38 \,\mu$ C/cm² was attained between about 116.0 °C and 115.5 °C by this sample during cooling. The observed E_c across the sample under the condition of saturation was 5.0 MV/cm.

On heating, the P_s, P_r and E_c of this $1.0 \,\mu$ m Ta/KNO₃/Ta sample exhibited the plots shown in Figure 4.42b. A gradual rise was observed in P_s and P_r as temperature increased until about 140.0 °C when an abrupt rise was seen. This rise in P_s and P_r continued until saturation was reached. E_c initially remained constant as temperature increased and about 140.0 °C, it exhibited a sharp drop in value. It stabilized again when maximum polarization was attained and remained at that value as P_s and P_r diminished. A P_r of $1.76 \,\mu$ C/cm² and a coercive field of 4.5 MV/cm developed across the sample during heating.



Temperature, T (°C)

(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.0 μ m KNO₃ thin film deposited on tantalum substrate.



(b) Variation of P_s,P_r and E_c with heating sample temperature for the 1.0 μm KNO3 thin film deposited on tantalum substrate.

Figure 4.41: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with changing sample temperature for $1.0 \,\mu m$, $1.3 \,\mu m$ and $1.5 \,\mu m$ Ta/KNO₃/Ta thin films.

4.2.24 Characteristic P-V Loop and J-V Curve of the Cooling $1.3 \mu m$ Ta/KNO₃/Ta Thin Film Sample

The characteristic P-V loops and J-V curves exhibited by the $1.3 \,\mu$ m Ta/KNO₃/Ta thin film sample during cooling are shown in Figures 4.42, 4.43 and Figure A.3b in Appendix A. Polarization switching peaks appeared in the J-V curve of the sample in the vicinity of 124.5 °C. As the sample cooled down further, the P-V loop developed into a P-V hysteresis loop though this loop remained unsaturated throughout the entire ferroelectric phase. The P-V hysteresis loop exhibited between 120.0 °C and 119.5 °C by this sample maintained the same loop shape irrespective of decreasing sample temperature. This signified the condition of maximum attainable polarization and a P_s of $0.35 \,\mu$ C/cm² was attained under this condition. The observed hysteresis and switching peaks were respectively no longer evident in the P-V loop and J-V curve below 65.5 °C.



Figure 4.42: 121.0 °C and 120.0-119.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu$ m KNO₃ thin film prepared on Ta.



Figure 4.43: 90.0 °C and 74.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.25 Characteristic P-V Loop and J-V Curve of the Heating $1.3 \,\mu$ m Ta/KNO₃/Ta Thin Film Sample

In Figures 4.44, 4.45 and Figure A.6b in Appendix A, the characteristic P-V loop and J-V curve exhibited during heating by the $1.3 \,\mu$ m Ta/KNO₃/Ta thin film sample are shown. As the sample temperature increased to about 110.0 °C, switching peaks were seen developing in the J-V curve while the P-V loop developed hysteresis. The P-V hysteresis loop though not well defined, increased with increasing temperature until the temperatures between 151.7 °C and 153.0 °C when it maintained the same loop shape. This was the condition of maximum possible polarization for this sample leading to a P_s of 0.38 μ C/cm². The hysteresis phenomenon of the P-V loop as well ad the J-V switching peaks disappeared above 155.5 °C.



Figure 4.44: 122.0 °C and 135.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.



Figure 4.45: 150.0 °C and 155.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.3 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.26 Temperature Dependence of P_s , P_r and E_c for the 1.3 μ m Ta/KNO₃/Ta Thin Film Sample

The P_s , P_r and E_c of the P-V hysteresis loop exhibited during the electric field heating and electric field cooling by the 1.3 μ m Ta/KNO₃/Ta thin film sample were also plotted against temperature to study their temperature dependence.

In the plots of Figure 4.47a, the temperature dependence of the P_s , P_r and E_c exhibited as the 1.3 μ m Ta/KNO₃/Ta thin film sample cooled are shown. With decreasing sample temperature, P_s and P_r increased while E_c decreased until the maximum possible attainable polarization was reached. Below the temperature of maximum polarization, P_s , P_r and E_c now decreased until the ferroelectric phase was no longer evident. As can be observed from the plot, a P_r of 0.33 μ C/cm² and a coercive field of 7.7 MV/cm existed across the sample at saturation between about 120.0 °C and 119.5 °C during cooling.

The temperature dependence of P_s , P_r and E_c for this 1.3 μ m Ta/KNO₃/Ta thin film sample as it was heated are shown in the plots of Figure 4.47b. From the plots, it can be seen that the P_s and P_r showed an initial gradual rise as temperature increased until about 140.0 °C when an abrupt rise occurred. This increase in P_s and P_r continued until maximum polarization was attained. E_c however increased with increasing temperature and stabilized after maximum polarization was attained. A P_r of $0.35 \,\mu$ C/cm² and a coercive field of 7.7 MV/cm occurred across the sample under this condition of saturation which occurred between the temperatures of 151.7 °C and 153.0 °C.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.3 μ m KNO₃ thin film deposited on tantalum substrate.

Figure 4.46: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with changing sample temperature for $1.0 \,\mu$ m, $1.3 \,\mu$ m and $1.5 \,\mu$ m Ta/KNO₃/Ta thin films.

4.2.27 Characteristic P-V Loop and J-V Curve of the Cooling $1.5 \,\mu$ m Ta/KNO₃/Ta Thin Film Sample

The characteristic P-V loop and J-V curve recorded as the $1.5 \,\mu$ m Ta/KNO₃/Ta thin film sample cooled through its ferroelectric phase are shown in Figures 4.47, 4.48 and Figure A.3c in Appendix A. The appearance of switching peaks in the J-V curve at about 121.5 °C characterized the onset of the ferroelectric phase. As the sample cooled further, the P-V loop exhibited hysteresis. The P-V hysteresis loop continued to develop as the sample cooled but however remained unsaturated all through the ferroelectric phase of this sample. Between the temperatures 115.0 °C and 114.0 °C the hysteresis loop remained unchanged in shape and this marked the condition of maximum possible polarization. This saturation condition resulted in a P_s of $0.44 \,\mu$ C/cm². The switching peaks which appeared in the J-V curve and the hysteresis nature of the P-V loop was no longer present below 50 °C.



Figure 4.47: 121.5 °C and 114.0 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.


Figure 4.48: 70.0 °C and 51.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the cooling $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.28 Characteristic P-V Loop and J-V Curve of the Heating $1.5 \,\mu$ m Ta/KNO₃/Ta Thin Film Sample

The characteristic P-V loops and J-V curves exhibited by the $1.5 \,\mu\text{m}$ Ta/KNO₃/Ta thin film sample are shown in Figures 4.49, 4.50 and Figure A.6c in Appendix A. An unsaturated hysteresis loop characterized the P-V loop recorded during heating. The P-V hysteresis loop which occurred between 151.5 °C and 153.0 °C remained unchanged and resulted in a P_s of $0.73 \,\mu\text{C/cm}^2$ as a result of this condition of maximum polarization.



Figure 4.49: 120.0 °C and 135.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.



Figure 4.50: 140.0 °C and 157.5 °C characteristic P-V hysteresis loops and J-V curves exhibited by the heating $1.5 \,\mu\text{m}$ KNO₃ thin film prepared on Ta.

4.2.29 Temperature Dependence of P_s , P_r and E_c for the 1.5 μ m Ta/KNO₃/Ta Thin Film Sample

 P_s , P_r and E_c of the 1.5 μ m Ta/KNO₃/Ta thin film sample exhibited the temperature dependence characteristics shown in the plots of Figure 4.52a. As P_s and P_r increased with decreasing temperature, E_c which was initially constant also decreased. This trend exhibited by these parameters continued until maximum possible polarization was attained. As temperature decreased below this region of maximum polarization, E_c exhibited a gradual decreased while P_s and P_r exhibited an abrupt drop until about 80.0 °C. At the low temperature region of the ferroelectric phase, P_s and P_r exhibited a gradual decrease until the ferroelectric phase was lost. A P_r of 0.40 μ C/cm² and a coercive field of 6.0 MV/cm were seen across the sample between the temperatures 114.0 °C and 110.0 °C during cooling.

The temperature dependence of P_s , P_r and E_c for this 1.5 μ m Ta/KNO₃/Ta sample observed during heating are depicted by the plots shown in Figures 4.52b. A general gradual rise was seen in P_s , P_r and E_c as temperature increased until about 140.0 °C when an abrupt increase was seen in P_s and P_r while a decrease was exhibited by E_c . This trend exhibited by these three parameters, continued until maximum possible polarization was reached. Above the temperature region where maximum polarization , P_s and P_r now decreased while E_c remained relatively constant. It can be observed from the plots that a P_r of 0.71 μ C/cm² and a coercive field 6.3 MV/cm existed across the sample between the temperatures of 151.5 °C and 153.0 °C during heating.



(a) Variation of P_s , P_r and E_c with cooling sample temperature for the 1.5 μ m KNO₃ thin film deposited on tantalum substrate.



(b) Variation of P_s , P_r and E_c with heating sample temperature for the 1.5 μ m KNO₃ thin film deposited on tantalum substrate.

Figure 4.51: Variation of spontaneous polarization P_s , remnant polarization P_r and coercive field E_c with cooling sample temperature for $1.0 \,\mu\text{m}$, $1.3 \,\mu\text{m}$ and $1.5 \,\mu\text{m}$ Ta/KNO₃/Ta thin films.

4.2.30 Comparison between P_s and P_r for the Ta/KNO₃/Ta Thin Film Samples obtained During Heating and Cooling

It is evident from the plots in the Figures shown in 4.53a, 4.53b, 4.53c and 4.53d that the P_s and P_r attained by the $1.0 \,\mu$ m Ta/KNO₃/Ta thin film sample was very large compared to those attained by the $1.3 \,\mu$ m and $1.5 \,\mu$ m Ta/KNO₃/Ta thin film samples. The ferroelectric phase exhibited by this $1.0 \,\mu$ m sample also extended over a much wider temperature range compared to that of the $1.3 \,\mu$ m and $1.5 \,\mu$ m samples which existed almost over the same temperature range.



(a) Variation of P_s with cooling sample temperature for the $1.0\,\mu$ m, $1.3\,\mu$ m and $1.5\,\mu$ m KNO₃ thin films deposited on tantalum substrate.



(c) Variation of P_s with heating sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on tantalum substrate.



(b) Variation of P_r with cooling sample temperature for the $1.0\,\mu\text{m}$, $1.3\,\mu\text{m}$ and $1.5\,\mu\text{m}$ KNO₃ thin films deposited on tantalum substrate.



(d) Variation of P_r with heating sample temperature for the 1.0 μ m, 1.3 μ m and 1.5 μ m KNO₃ thin films deposited on tantalum substrate.



4.3 P_s, P_r and E_c at Maximum Possible Attainable Polarization

From the results obtained from the P-V hysteresis loop measurements it can be noted that, for every sample, there existed a temperature range during both the heating and cooling cycles where maximum possible attainable polarization occurred. Within this temperature range, the observed hysteresis loop maintained a constant loop shape irrespective of changing sample temperature. Table 4.2 and 4.3 show the exhibited P-V hysteresis loops and their associated P_s, P_r and E_c attained under the condition of maximum polarization during both the heating and cooling run. From these tables, the following observations were significant. The 1.0 μ m Ni/KNO₃/Ni thin film sample produced the highest P_s (4.12 μ C/cm²) during the cooling experimental run whilst the $1.0 \,\mu m$ SS/KNO₃/SS thin film sample produced the highest P_s (3.75 μ C/cm²) during the heating experimental run. This 1.0 μ m SS/KNO₃/SS thin film sample also produced the highest P_r of $3.30 \,\mu$ C/cm² during heating while both the $1.0 \,\mu\text{m}$ Ni/KNO₃/Ni and $1.0 \,\mu\text{m}$ SS/KNO₃/SS thin film sample recorded the highest P_r of $2.88 \,\mu\text{C/cm}^2$ during the cooling cycle. The Ta/KNO₃/Ta samples generally exhibited the weakest P-E hysteresis loops thus producing the lowest P_s and P_r values during both cycles. The P-V hysteresis loops exhibited by the Ni/KNO₃/Ni and SS/KNO₃/SS thin film samples were well defined and square-like in shape.

Sample	Thickness	Temperature	Hysteresis Loop	Ps	Pr	Ec
	μm	Range °C		μC/cm ²	μC/cm ²	MV/cm
	1.0	106.0 - 105.5	5.00 6 7 123 a 123 -135 -10 -13 -10 -13 -10 -13 -10 -10 -10 -10 -10 -10 -10 -10	4.12	2.88	5.0
Ni/KNO ₃ /Ni	1.3	110.9 - 106.5	2 500 (1) 210 a 0.055 1,230 a 0.055 1,230 	2.44	2.15	5.8
	1.5	112.4 - 110.5	500 3175 4 125 - 125 - 250 - - 250 - - 25 - 20 - 45 - 20 - 5 - 0 - 5 - 10 - 15 - 20 - 25 Applied Voltage (V)	2.65	2.34	5.0
SS/KNO ₃ /SS	1.0	126.0 - 120.5	5.00 6 9 9 9 9 9 9 9 9 9 9 9 9 9	3.38	2.88	6.0

Table 4.2: Characteristics of the region of maximum polarization recorded during the cooling of the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta thin film samples.

Cont'd on next page.

Sample	Thickness	Temperature	Hysteresis Loop	Ps	Pr	Ec
	μm	Range °C		μC/cm ²	μC/cm ²	MV/cm
SS/KNO ₃ /SS	1.3	116.2 - 113.9	5.00 3.75 2.30 1.23 -1.25	2.90	2.69	5.4
	1.5	120.0 - 116.0	5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.50 5.125 5.50 5.125 5.50 5.125 5.50 5.125 5.50 5.125 5.50 5.125 5.50 5.125 5.10	2.56	2.40	5.3
	1.0	116.5 - 115.5	2 500 G 1873 G 0625 - -25 -20 -15 -10 -5 0 5 10 15 20 25 Applied Voltage (V)	2.38	1.38	5.0
Ta/KNO ₃ /Ta	1.3	120.0 - 119.5	5000 2560 a 1250 - 25500 -	0.35	0.33	7.7
	1.5	114-110.0.0	275-0 275-0 a, 125-0 	0.44	0.40	6.0

Table 4.2 Cont'd

Sample	Thickness μm	Temperature Range °C	Hysteresis Loop	P_s $\mu C/cm^2$	P_r $\mu C/cm^2$	E _c MV/cm
	1.0	152.6-154.5	5.00 4.125 0 -1.25 -0 -1.25 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0	3.15	2.74	4.9
Ni/KNO ₃ /Ni	1.3	148.5 - 149.2	2 500 1.875 1.250 0 0 0.625 -1.250 -1.250 -1.250 -1.250 -1.250 -1.255 -1.250 -1.255 -1.250 -1.255 -1.25	1.76	1.54	6.9
	1.5	155.0 - 157.0	5.00 F 2.30 a 125 -2.5 20 45 -10 5 10 15 20 25 Applied Voltage (V)	2.63	2.26	5.2
SS/KNO ₃ /SS	1.0	167.0 - 171.0	5.00 4.125 3.13 -1.25 -2.5 -20 -15 -10 -5 -0 -5 -10 -15 -20 -25 Applied Voltage (V)	3.75	3.30	5.0

Table 4.3: Characteristics of the region of maximum polarization recorded during the heating of the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta thin film samples.

Cont'd on next page.

Sample	Thickness μm	Temperature Range °C	Hysteresis Loop	P_s $\mu C/cm^2$	P_r $\mu C/cm^2$	E _c MV/cm
SS/KNO ₃ /SS	1.3	146.5 - 150.0	5.00 1.25 0 -1.25 -2.50 -2.50 -2.5 -20 -15 -10 -5 -10 -15 -20 -25 Applied Votage (V)	3.15	2.80	5.0
	1.5	154.2 - 158.9	250 4.125 -1.25 -2.50 -1.25 -2.50 -2.5	2.88	2.60	4.8
	1.0	160.0 - 163.0	5.00 G 2.20 4.125 -2.20 -1.25 -2.20 -	1.88	1.76	4.5
Ta/KNO ₃ /Ta	1.3	151.7 - 153.0	151.7 °C - 153.0 °C 375.0 a. 125.0 -250.0 -250.0 -25.00	0.38	0.35	7.7
	1.5	151.5 - 153.0	1250 - 153.0 °C	0.73	0.71	6.33

Table 4.3 Cont'd

4.4 Optical Characterization of KNO₃

The optical absorbance spectra as a function of wavelength in the range of 300 to 750 nm were obtained for KNO₃ thin films deposited on glass substrates at temperatures of 480 °C and 520 °C. Figure 4.53 shows the absorbance spectra for these samples. A careful observation of the spectra revealed the absorption edge of the optical system occurred in the spectral range of 300 to 340 nm. Absorption coefficient values were determined at every 5 nm change in wavelength using equation 2.57. For the high absorption region where α obeys equation 2.58, Tauc plots were obtained for both allowed direct and allowed indirect transitions and these are shown in Figure 4.54a and Figure 4.54b respectively. An



Figure 4.53: Absorbance spectra of KNO_3 thin films deposited at temperatures of 480 °C and 520 °C.

extrapolation of the linear regions of the curves to the energy axis $\hbar\omega$, yielded the optical bandgap energies given in Table 4.4. Urbach plots (Figure 4.55) of the sample were obtained



Figure 4.54: Tauc plots of KNO_3 thin films deposited at 480 °C and 520 °C.



Figure 4.55: Urbach plots of KNO₃ thin films deposited at 480 °C and 520 °C.

by plotting $\ln \alpha$ as a function of energy $\hbar \omega$. The Urbach energy (E_u) values (see Table 4.4) obtained for the samples were determined from the gradients of the linear portions of the Urbach plots.

Table 4.4: Optical bandgaps of allowed direct E_g^d , allowed indirect transitions E_g^i and Urbach Energies E_u of KNO₃ thin films deposited at 480 °C and 520 °C

Temperature of Deposition (°C)	Allowed direct bandgap E_g^d (eV)	Allowed indirect bandgap E_g^i (eV)	Urbach energy <i>E_u</i> (eV)
480	3.79	3.50	0.302
520	3.76	3.37	0.380

CHAPTER 5

DISCUSSIONS

5.1 Substrate Electrode Effect on Ferroelectric Properties

Ferroelectricity in KNO₃ is a consequence of the shift of the NO₃⁻ group from the centre of the rhombohedral unit cell of phase III. With the NO₃⁻ group being off-centre, it follows the reversal of the external electric field jumping between both the positive and negative positions (Sawada et al., 1961; Murugan et al., 1999). The reversal nature of the NO₃⁻ group of KNO₃ consequently results in hysteresis. P-V hysteresis is one of the key characteristics of the phenomenon of ferroelectricity as was the case of the KNO₃ ferroelectric samples studied in this work.

The hysteresis phenomena exhibited by the P-V loops as well as the polarization switching peaks which appeared in the J-V curves of each studied KNO_3 thin film sample signified the presence of ferroelectricity in the samples. From the results obtained from the P-V and J-V measurements, it can be observed that the above mentioned characteristics of the P-V and the J-V curves occurred only within a certain temperature range. This is an indication that KNO_3 is ferroelectric only within a certain temperature range. Above or below this temperature range, it exhibits paraelectric characteristics and thus behaves like a normal dielectric. It is also noted in this work that, irrespective of the substrate electrode on which the KNO_3 thin film was deposited, every sample exhibited ferroelectricity within a certain

temperature range.

The films deposited on SS and Ni exhibited the best P-V hysteresis loops while those prepared on Ta exhibited the worse. The hysteresis loops obtained with the SS and Ni substrates were very well defined but the films prepared on Ta exhibited unsaturated hysteresis loops almost the entire duration of the ferroelectric phase of the sample.

The nature of the P-V hysteresis loop exhibited by the SS/KNO₃/SS, Ni/KNO₃/Ni and Ta/KNO₃/Ta samples and the temperature range over which these P-V hysteresis loops extended and existed have revealed the possibility of stabilizing and extending the ferroelectric phase of KNO₃ thin films by means of an appropriate substrate electrode. Well-defined hysteresis loops characterized the ferroelectric of the KNO₃ thin films prepared on SS and Ni but unsaturated hysteresis loops were observed for the films deposited on Ta. For these film samples prepared on Ta, the onset and existence of the ferroelectric phase was more often determined by the presence of switching peaks in the J-V curves of the samples.

In considering the temperature range over which the P-V hysteresis loop occurred, SS was noted to stabilize and extend the ferroelectric phase beyond room temperature while Ni stabilized and extended the phase close to room temperature. Ta also extended the phase to lower temperatures; however it was observed that polarization in the KNO₃ film layers were severely degraded leading to poorly defined P-V hysteresis loops compared with the hysteresis loops of the films prepared on SS and Ni which were well defined throughout the existence of the ferroelectric phase.

These observations regarding the nature of the exhibited P-V hysteresis loops can be explained in terms of the nature of the currents present in the KNO_3 ferroelectric capacitor sample. Real capacitors are known to compose of two sources of current: displacive current

 $\left(\frac{\partial D}{\partial t}\right)$ and leakage current $\left(J_{1}\right)$ (Meyer et al., 2005). The observed hysteresis loops can therefore be explained in terms of displacive current and leakage current. The hysteresis loop exhibited by ferroelectric capacitors is as a result of the $\frac{\partial D}{\partial t}$ component of the current while J₁ is the component responsible for inflating the loop (Meyer et al., 2005). That is, the presence of the leakage current results in the altering of the hysteresis loop in the sense that it inflates it till it looks elliptical. Increasing amounts of leakage current within the film can thus inflate its ferroelectric hysteresis loop to the point of no evidence of hysteresis, even at maximum polarization. Displacive current is therefore the desirable component between the two possible sources of current since P-V hysteresis is a necessary feature that confirms the presence of ferroelectricity.

The presence of leakage current in ferroelectric thin films can be due to oxygen vacancies at the metal/film interface. It can as well be due to electronegativity as well as electron configuration and the potential barrier heights at the metal/film interface.

According to Schottky (1938), a barrier known as Schottky barrier develops at semiconductor/metal interface when wide bandgap semiconductors come in contact with metals (Blom et al., 1994). The bandgap value analysed using UV-visible absorption spectroscopy indicates that KNO₃ is a wide bandgap semiconducting ferroelectric with a bandgap value of 3.79 eV. It therefore follows from this argument that when the KNO₃ thin film came in contact with the Ni, SS and Ta substrate electrodes respectively, a Schottky barrier developed at the interface between the film and the substrate electrode. Schottky theory however defines two limits, which are the Schottky limit, equivalent to the Electron Affinity rule, and the Bardeen limit (Demkov and Navrotsky, 2005). The Electron Affinity rule states that vacuum levels of two materials forming a heterojunction should be lined up

(Borisenko and Ossicini, 2008). That is, the conduction band offset at such a junction is given by the difference in the electron affinities of the materials (Demkov and Navrotsky, 2005). This model was invoked by Schottky to explain the barrier heights of metal-semiconductor contacts, also called Schottky contacts, proposing that the barrier height Φ is given by $\Phi =$ $W - \tau$ (Schubert, 2003), where W is the work function and τ is the electron affinity. However, this model fails to explain the barrier heights in metal-semiconductor (metal-ferroelectric) contacts (Schubert, 2003; Pintilie et al., 2008).

On the other hand, Bardeen (1947) showed that $W - \tau$ does not play a substantial role in explaining the barrier heights of metal-semiconductor contacts. He showed that, instead, interface dipoles caused by charged interface states determine the barrier height of metal-semiconductor contacts (Bardeen, 1947; Schubert, 2003). Thus in the Bardeen limit, the potential barrier is totally controlled by the density of the interface states D_{it} (Pintilie et al., 2008). The interface states are considered through a factor *S*, which describes the degree of alignment caused by the interface states (Demkov and Navrotsky, 2005). *S* is defined in terms of κ , the dielectric constant of the ferroelectric (semiconductor) material as (Demkov and Navrotsky, 2005):

$$S = \frac{1}{1 + 0.1(\kappa_{\infty} - 1)^2}$$
(5.1)

The *S* factor is unity in the case of the Schottky limit and it is zero in the case of the Bardeen limit (Pintilie et al., 2008), though in real systems, 0 < S < 1. Knowing the *S* factor and the thickness of the interface layer, D_{it} can be estimated (Sze and Ng, 2007). However, the *S* factor is not dependent on the metals but on the ferroelectric material primarily (see equation 5.1) (Sze and Ng, 2007), and therefore, should be approximately the same for all substrate

electrodes. The above explains the source of the potential heights existing in the metal/ KNO_3 interfaces. However, it does not fully explain the behaviour of the leakage current which is the suspected cause of the variation in the P-V and J-V characteristics among the KNO_3 films prepared on the three different substrate electrodes.

In addition to the interface state densities and metal work function, the leakage current behaviour is attributed to oxygen vacancies at the metal/film interface. Accumulation of oxygen vacancies V_o at the metal/film interface has been identified to degrade the polarization in ferroelectric thin films during field cycling (Duiker et al., 1990). Notwithstanding, it has been found that smaller concentration of V_o at the interface would reduce injection of electronic carriers into the film, and consequently prevent polarization loss (Damjanovic, 1998). However, as the oxygen-deficient regions grow into the bulk, they effectively screen part of the film from the applied field, and this leads to polarization loss (Scott et al., 1991). Yoo and Desu (1992) have reported that entrapped V_o can cause structural damage at the metal/film interface that can also lead to loss of polarization. It has been further suggested that creation of an oxygen-vacancy-rich region at the metal/film interface may lead to the formation of an n-type layer near the interface (Al-shareef et al., 1997). The presence of this layer increases the electron injection rate in the film during field cycling. These injected electronic carriers may get trapped at the domain walls leading to domain-wall pinning and polarization suppression (Damjanovic, 1998). Finally, Stancu et al. (2008) report that in ferroelectric films, V_o act as donors and hence result in high leakage current.

The presence of leakage current in a capacitor sample has also been associated with the electronegativity of the electrode in contact with the film (dielectric). Leakage current density increases as electrode electronegativity decreases (Pintilie et al., 2008). Though, at

this time, the value of the electronegativity of 304 austenitic stainless steel is not known, Eastern Foundry Limited (2005) places its chemical potential¹ below that of Ni. This implies that the electronegativity of 304 austenitic stainless steel is higher than that of Ni and Ta. The ranking order of the electronegativity for the SS, Ni and Ta substrate electrodes are shown in Table 5.1. From this order of arrangement of the electronegativity of these substrate electrodes, it is expected that the samples formed with SS will exhibit the least effect of leakage current while the samples formed with Ta will exhibit the largest effect of leakage current.

Substrate Electrode	Electronegativity (Pauling Scale)
SS	N/A
Ni	1.91
Та	1.5

Table 5.1: Electronegativity descending order ranking of 304 stainless steel (SS), Nickel (Ni) and Tantalum (Ta).

It is seen from the P-V hysteresis loops and the J-V curves that the films deposited on Ta experienced the largest effect of leakage current. As a consequence of the leakage current effect dominance in Ta/KNO₃/Ta samples, the hysteresis loops exhibited by the films were not evident at certain stages of the ferroelectric phase. The high presence of leakage current in Ta can be ascribed to accumulation of oxygen vacancies at the KNO₃/Ta interface as well as its low electronegativity relative to Ni and SS. The oxygen vacancies are believed to have been created during the deposition of the thin films. Ta⁵⁺ ions are believed to have diffused into the KNO₃ and bonded with O^{2-} ions to form Ta₂O₅. This bonding may have created a lot of oxygen vacancies V_o at the interface layer of the KNO₃/Ta which is believed to have

¹The chemical potential of an atom is sometimes said to be the negative of the atom's electronegativity

contributed to the poor hysteresis loops exhibited by Ta/KNO₃/Ta samples.

The SS/KNO₃/SS samples however exhibited very well-defined P-V hysteresis loops because it is believed that these samples suffered virtually no leakage current effect. This led to a stabilized and sustained ferroelectric phase over a wide temperature range with a well-defined hysteresis loop even at room temperature. The minimal leakage current effect can be linked to the stainless steel's (SS) composition as an alloy. SS has been known to have some oxygen dissolved in it and is therefore able to act as an oxygen reservoir or a sink for oxygen vacancies (Nanjo et al., 1997). Thus, the oxygen present in SS filled any oxygen vacancies that existed at the metal/film interface (Stancu et al., 2008). As a result, V_o was almost absent at the KNO₃/SS interface. It is also evident that since SS comes first, moving down the electronegativity table shown in Table 5.1, it least enhanced leakage current amongst the three substrate electrodes.

Elevated temperature deposition conditions could have caused the created of oxygen vacancies V_0 at the Ni/KNO₃ interface through the formation of nickel oxide (i.e. NiO). This bonding process involves one O^{2-} ion and one Ni²⁺ ion compared to five O^{2-} ions required to form Ta₂O₅ with two Ta⁵⁺. Therefore, in comparison, the amount of V_0 that would be created at the Ni/KNO₃ interface is expected to be much less than that created at the Ta/KNO₃ interface. This suggests that, the density of leakage current at the Ni/KNO₃ interface would be small. It is understood from Damjanovic (1998) that this small concentration of oxygen vacancies act to reduce the injection of electronic charge carriers into the KNO₃ film, and enhance polarization, and thus the formation of the well-defined P-V hysteresis loops exhibited by the Ni/KNO₃/Ni samples. Also, the placement of the electronegativity of Ni, as shown in Table 5.1, between SS and Ta confirms that the effect of leakage current on the Ni/KNO₄/Ni sample should be minimal compared to Ta/KNO₃/Ta sample, whilst performing

poorly with respect to the SS/KNO₃/SS sample, since leakage current is known to increase as electronegativity decreases.

Pintilie et al. (2008) states categorically that there is a clear dependency of leakage current on the occupancy state of the d-shell; the metal/semiconductor interface of metals with complete d-shell have the lowest leakage current. Table 5.2 show the electron configuration for Ni and Ta. The electron configuration of stainless steel is not known at this point. The d-shell of Ni is filled with 8 electrons and forms very good rectifying contacts on the KNO₃ films as opposed to Ta with only 3 electrons in the d-shell and thus, forming ohmic contacts more readily. Since ohmic contacts allow the free flow of current, it is believed that it enhanced the leakage current flow in the Ta/KNO₃/Ta samples. On the other hand, the rectifying nature of the Ni/KNO₃ contact might have suppressed the leakage current flow in the Ni/KNO₃/Ni samples. This indicates why the hysteresis loops exhibited by the Ni/KNO₃/Ni samples were also very well-defined. This also indicates that though the electron configuration of 304 austenitic stainless steel may not be known at this point, its d-shell may be more filled than Ni.

Substrate Electrode	Electron Configuration
SS	N/A
Ni	$Ar3d^84s^2$
Та	$Xe4f^{14}5d^36s^2$

Table 5.2: Electron configuration of Ni and Ta.

5.2 Substrate Electrode Effect on Phase Transition Characteristics

The dielectric susceptibility of normal dielectrics decreases monotonously with decreasing temperature. In contrast to this, the dielectric susceptibility of a ferroelectric in the non-polar phase increases with decreasing temperature, passes through a sharp maximum at the transition temperature, and then decreases when the spontaneous polarization begins to rise (Seitz and Turnbull, 1957).

For ferroelectrics, dielectric constant ε_r is approximately equal to susceptibility (see page 28). Based on this characteristic, dielectric susceptibility curves which express polarization behaviour of ferroelectrics can be replaced with dielectric constant curves. ε_r of ferroelectrics is severely affected by transition from one phase to another phase (example, transition from a paraelectric phase to a ferroelectric phase). It is thus a material property that can be used in studying phase transition characteristics of ferroelectrics. This can be done by obtaining certain parameters associated with the region of anomaly which occurs in the temperature dependence curves of the dielectric constant ε_r and inverse dielectric constant (dielectric stiffness) $\frac{1}{\varepsilon}$.

Dielectric stiffness $\left(\frac{1}{\varepsilon_r}\right)$ temperature dependence curve of a normal ferroelectric follows the well-known Curie-Weiss law (Lines and Glass, 1977) in the vicinity of temperatures just above the transition temperature, T_c. By obtaining the temperature corresponding to the dielectric constant which occurs at the sharp maximum, the transition temperature also referred to as Curie point T_c can be known. The anomalous behaviour of the curve in the region of T_c also makes it possible to determine the Curie constant C as well as the Curie temperature T_o using the Curie-Weiss relation given in equation 2.48 (see page 65). Since the region just above T_c obeys the Curie-Weiss law and is thus linear, an extension of this linear portion of the curve to the temperature axis yields T_o . The value of T_c and T_o is used to determine the order of the paraelectric-ferroelectric transition. When $T_c \neq T_o$, it is indicative of a first-order transition while $T_c = T_o$ is the case for a second-order transition. The Curie constant is obtained from the inverse of the gradient of the linear portion used in determining T_o . The type of the ferroelectric transition is determined using the order of the Curie constant C. An order of 10³ is indicative of an order-disorder transition while an order of 10⁵ signify a displacive transition (Nkum, 1989).

The $\frac{1}{\varepsilon_r}$ temperature dependence behaviour plots obtained for the samples used in this work showed that $\frac{1}{\varepsilon_r}$ followed the Curie-Weiss behaviour in the paraelectric phase. It was observed from the ε_r temperature dependence plots that, ε_r rose to a sharp maximum at T_c as temperature decreased and afterwards decreased as temperature further decreased. The nature of the anomalous behaviour of the curves signified that an abrupt structural transition occurred at the paraelectric-ferroelectric phase transition. The obtained Curie point T_c and the Curie temperature T_o were observed to be the same (T_o = T_c) as can be seen from Table 4.1. This observation meant that every thin KNO₃ film layer studied in this work exhibited a second-order phase transition regardless of the substrate electrode on which it was deposited.

The second-order phase transition which characterized the paraelectric to ferroelectric phase transitions of the thin film samples can be ascribed to the restraint of the misfit strain due to the rigidity of the substrate (Zheng et al., 2007). Misfit strains can be imparted into thin films through differences in lattice constants and thermal expansion behaviour between the film and the underlying substrate (Schlom et al., 2007). The thermal expansion behaviour results in thermal stress which is as a result of depositing films at elevated temperatures and cooling

to room temperature. After the film/substrate system has cooled, the large mismatch between the thermal expansion of the substrate and film produces a state of equi-biaxial compression in the film. In the case of the lattice mismatch, the deposited thin film is strained to have the same interatomic spacing as the substrate (Ohring, 1992).

KNO₃ has a thermal expansion coefficient and lattice constant of 1.5×10^{-4} /°C (Sao and Tiwary, 1981) and 5.266 Å (Aydinol et al., 2007) respectively and in Table 5.3, the thermal coefficients and lattice constants of the substrate electrodes are shown. It is seen from this table (Table 5.3) that, a large misfit strain was present in the film as a result of the thermal expansion coefficient differences as well as lattice constant differences between the film and substrate electrodes.

C	and tantardin. a and a values were picked from nandbooks.					
	Substrate	Lattice Constant a (Å)	Lattice Misfit l_f	Thermal Expansion Coefficient α (×10 ⁻⁶ /°C)	Thermal Stress σ_f (×K × 10 ⁻²) GPa	
	Ni	3.52	0.332	13.0	-1.370	
	SS	3.58	0.320	17.3	-1.327	

6.5

-1.435

0.371

Ta

3.31

Table 5.3: Lattice constant, *a*, and thermal expansion coefficient α of nickel, stainless steel and tantalum. α and *a* values were picked from handbooks.

From equation 2.5 (page 21) the thermal stress σ_f in the film can be given as $\sigma_f = K(\alpha_s - \alpha_f)$, where K is a constant defined as $\frac{\Delta T E_f}{(1 - v_f)}$, and ΔT is change in temperature. E_f and v_f are the Young's modulus and Poisson ratio of KNO₃ respectively. Lattice constant differences between a substrate and a deposited film layer also results in lattice misfit given as $(l_f = \frac{(\alpha_f - \alpha_s)}{\alpha_f})$ where α_f and α_s are the lattice constants of the film and the substrate respectively. The resulting l_f and σ_f as seen in Table 5.3 are significant and were considered as the source of the misfit strain which caused the second-order phase transition that characterized the paraelectric-ferroelectric transition of these ferroelectric KNO₃ samples used in this work.

It is evident from Table 5.4 that the samples studied in this work underwent an order-disorder transition. This is linked to the 10^3 order Curie constant values attained by the samples.

Comula	Curie Constant C	
Sample	$\times 10^3 \mathrm{K}$	
Ni/KNO ₃ /Ni	1.5218	
SS/KNO ₃ /SS	4.5351	
Ta/KNO ₃ /Ta	0.7573	

Table 5.4: Curie constants obtained for some selected KNO₃ thin film samples.

5.3 Polymorphic Transitions of KNO₃

All the SS/KNO₃/SS, Ni/KNO₃/Ni and Ta/KNO₃/Ta thin film samples exhibited polymorphic transitions as is characteristic of KNO₃ irrespective of the substrate electrode. During cooling of the sample, the high temperature phase I possessing a trigonal structure with the nitrate groups orientationally disordered in calcite-type positions transformed into phase III possessing another trigonal structure which has the nitrate groups ordered in aragonite-type positions. As the samples cooled further, phase III then transformed into phase II possessing an orthorhombic structure (Yanagi, 1965).

Since cooling rate affects the appearance of phase III it is believed that the cooling rate

of 0.5° C/min used favoured the development of the very well established ferroelectric phase exhibited by the studied samples. For the Ni/KNO₃/Ni and Ta/KNO₃/Ta samples, the transition from phase I to phase III occurred between about 120.0 °C and 124.0 °C in agreement with what has been reported by (Chen and Chernow, 1967; Kawabe et al., 1965; Westphal, 1993; Dabra et al., 2009). For the 1.0 μ m Ni/KNO₃/Ni and Ta/KNO₃/Ta samples, the transition of phase III to phase II was however extended to ≈ 40.0 °C for the Ni/KNO₃/Ni and ≈ 50.0 °C for the Ta/KNO₃/Ta in comparison with ≈ 100.0 °C attained by the bulk form.

In the case of the $1.0 \,\mu\text{m}$ SS/KNO₃/SS samples, both the transition from phase I to phase III and from phase III to phase II were extended. The phase I to phase III transition temperature was extended to ≈ 148.0 °C while the phase III to phase II transition temperature extended beyond room temperature since at room temperature hysteresis was still evident in the P-V loop.

Though a phase II to phase I transformation was expected for the heating experimental run under atmospheric pressure, the intermediate phase III appeared on heating from room temperature. This is attributed to the heating rate of 1.7°C/min used during the measurements. This is believed to have reduced the effect of thermal agitation and favoured the alignment of dipoles.

5.4 P_s , P_r and E_c Temperature Dependence

As a consequence of some order in the alignment of electric dipoles, ferroelectrics pass from a non-polar phase to a polar phase as they cool through the Curie point (T_c). Electric dipoles can also be created as temperature changes and these dipoles may align below T_c . The ordering tendency of dipoles is influenced by temperature. Above T_c , it is disrupted by thermal agitation while electric field influences it below and above T_c . Dipole ordering is less strongly opposed by thermal agitation with decreasing temperature.

The sharp rise in P_s and P_r which occurred just after a brief gradual increase below T_c can be attributed to large ordering of the dipoles in the direction of the applied electric field as temperature decreased. This was an indication that thermal agitation influenced the dipole ordering less and less as temperature decreased. Polarization saturation effect prevailed over thermal effects below T_c .

With increasing temperature, the thermal motion of atoms increases and thus, they eventually overcome the energy barrier separating the various orientations. As temperatures reach very high values however, atomic distribution becomes statistical and the dielectric behaves as a normal dielectric and no longer as a polar material (Tilley, 2004).

The temperature dependence characteristics of P_s and P_r exhibited during heating showed that the thermal motion effect on the atoms favoured dipole alignment. With a relatively slow heating rate of 1.7°C/min, the dipoles aligned in the direction of the applied electric field as temperature increased leading to the steady gradual rise exhibited by P_s and P_r . The sharp rise that was seen in these parameters can be attributed to a large alignment of energetically favoured dipoles and also the reduction of the E_c across the sample with increasing temperature.

5.5 T_c Shift in SS/KNO₃/SS Thin Film Samples

Though the T_c of the KNO₃ thin films prepared on Ni and Ta are in good agreement with the reported inherent Curie point (T_c) of KNO₃, it can be noted from Table 4.1 that the films

prepared on SS had their T_c's shifted from the reported inherent T_c (between ≈ 120 °C and 124 °C) (Westphal, 1993; Chen and Chernow, 1967; Kawabe et al., 1965; Dabra et al., 2009) to above 140 °C.

The cause of such shifts in the T_c of ferroelectric materials is linked to strong polarization-strain coupling (Schlom et al., 2007). Strain-induced enhancements in T_c as large as tens of degrees have been observed in strained ferroelectric thin films (Schlom et al., 2007). The origin of the strain could be the mismatch between lattice constant and/or thermal expansion coefficient of the film and the underlying substrate, or they can arise from defects formed during film deposition as reported by Schlom et al. (2007). It should however be noted as Damjanovic (1998) reports that, it is difficult to predict exact values of strain because stress relaxation mechanism due to film/substrate interface and imperfections are usually unknown.

The misfit strain and thermal stress in the film deposited on Ni and Ta (see Table 5.3) do not quite agree that the origin of T_c shifts observed in the films prepared on SS are lattice constants mismatch and/or thermal expansion coefficients mismatch between the film and the substrates. It can be observed from the table that the misfit strain imparted into the films are closely related. This indicates that, a shift in T_c should have been observed for all films if the strain responsible for the shift was due to the lattice constants mismatch and/or thermal expansion behaviour between the film and the underlying substrate.

There is a possibility of chemical interdiffusion across an interface during deposition at elevated temperatures (Jia et al., 2002). The presence of Fe^{3+} ions in ferroelectric materials have been reported to greatly influence the T_c of certain ferroelectric thin films (Maier et al., 2001). In some cases, this has resulted in the shifting of the inherent T_c to temperatures

far exceeding what has been reported for their bulk counterparts (Kumar et al., 2010). Consequently, a more viable explanation for the occurrence of T_c shift in the films prepared on SS arise from lattice defects due to diffusion of Fe ions from SS into the KNO₃ films during deposition. Fe³⁺ is usually referred to as an interstitial ion due to its ionic radius of 0.645 Å (Li et al., 2002b). As a result of this characteristic, it is believed that Fe³⁺ diffused into and filled interstitial sites of the KNO₃ film layer during deposition.

Though interstitial ions such as Fe^{3+} are much smaller than the host material, they are usually bigger than the interstitial site they occupy. As a result, the lattice of the host material must deform to accommodate them, leading to defects in the deposited film structure. According to Schlom et al. (2007), defects which are usually formed during film deposition can impart strain. This is believed to be the source of the strain that coupled with polarization and caused the shift in T_c of the films prepared on SS.

5.6 Effect of Differences in KNO₃ Film Layer Thickness

It was thought that ferroelectricity was suppressed in small particles and thin films (Lines and Glass, 1977). The situation however changed after experiments have identified ferroelectric ground states in 40 Å perovskite oxide films (Tybell et al., 1999) and in 10 Å thick crystalline copolymer films (Bune et al., 1998). Ferroelectricity in KNO₃ is known to improve with decreasing thickness (Scott et al., 1987; Aydinol et al., 2007).

An enhancement in the ferroelectric property of the films prepared on SS was observed, as can be seen in the temperature dependence plots of P_s and P_r for the SS/KNO₃/SS samples. The plot for the 1.3 μ m, though closely related to that of the 1.5 μ m layer, still showed considerable improvement in P_s and P_r . The plot for the 1.0 μ m thin film layer shows significantly that reduction in film thickness enhances the ferroelectric property of KNO_3 . An extension of the lower temperature end of the ferroelectric phase of KNO_3 beyond room temperature was achieved with the stainless steel substrate electrode.

The films prepared on Ni and Ta did not exhibit exactly the same trend as seen in the film layers prepared on SS. For these samples, the P_s and P_r attained by $1.5 \,\mu$ m layers were higher than that of the $1.3 \,\mu$ m film layers. The P_s and P_r of the $1.0 \,\mu$ m thin film layer, just like in the case of SS, however, recorded improvement over the $1.3 \,\mu$ m and $1.5 \,\mu$ m layers. These observations made on the thin film layers deposited on Ni and Ta also generally indicate that thinner KNO₃ films of dimension of $1.0 \,\mu$ m thick did enhance the ferroelectric properties of KNO₃.

Empirically, the coercive field E_c which characterizes polarization reversal in a ferroelectric film, usually increases significantly with decreasing film thickness. The observation made on the 1.0 μ m thin film layers confirmed this fact. This can be drawn from the coercive field relation given as $E_c = \frac{V}{d}$ where V and d are the coercive voltage and dielectric layer thickness respectively. Since E_c and d are inversely related, it follows that as film thickness reduces, E_c increases. The large coercive field values obtained for the KNO₃ film layers prepared on Ta can partly be attributed to the large leakage current effect on the samples.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this thesis, the possibility of using substrate electrodes to stabilize the ferroelectric phase exhibited by KNO_3 thin films has been investigated. These investigations were carried out using nickel (Ni), stainless steel (SS) and tantalum (Ta) metals as substrate electrodes. The results obtained from this work have established the possibility of stabilizing the ferroelectric phase of KNO_3 with substrate electrodes. It was observed that the choice of substrate electrode was paramount in the quest to stabilize and enhance the ferroelectric phase of KNO_3 thin films. It was revealed that for a given range of substrate electrodes, a given KNO_3 thin film would exhibit varied ferroelectric properties.

The results obtained from polarization-voltage (P-V) measurements as well as the current density-voltage (J-V) measurements revealed that the SS and Ni substrate electrodes better supported the ferroelectric phase exhibited by the deposited KNO₃ thin film. Very well-defined P-V hysteresis loops were displayed by these thin KNO₃ film layers prepared on the SS and Ni substrate electrodes. However, between the films prepared on SS and the films prepared on Ni, those prepared on SS gave the best results in terms of stabilizing and extending the ferroelectric phase. The ferroelectric phase exhibited by the 1.0 μ m SS/KNO₃/SS film sample was stabilized such that it existed even at room temperature but

this was not the case for the $1.0 \,\mu\text{m}$ Ni/KNO₃/Ni film sample. The Ta/KNO₃/Ta film samples however generally exhibited poorly defined unsaturated hysteresis loops even under the condition of maximum polarization.

The observed variations in the exhibited P-V hysteresis loops were attributed to leakage current. The existence of potential barrier at the metal/film interface, the presence of oxygen vacancies at the interface as well as the electronegativity and the electron configuration of the substrate electrode were seen to be the possible sources of leakage current in the thin films.

An optical bandgap value of about 3.79 eV analysed using UV-visible absorption spectroscopy have shown that KNO₃ is a wide bandgap semiconducting ferroelectric. With KNO₃ being a wide bandgap semiconductor, a film-metal interaction leading to the creation of a potential barrier is expected to occur when the film and the metal electrodes are brought together. This potential barrier was found to be as a result of interface dipoles caused by charged interface states. The potential barrier was thus totally controlled by the density of the interface states. The barrier height of a semiconductor/metal interface reduces the effect of leakage current existing at the interface. This suggests that the barrier height in KNO₃/SS is higher than KNO₃/Ni and KNO₃/Ni higher than KNO₃/Ta. Generally, for a lower barrier height at the metal/semiconductor interface, there is an associated higher leakage current.

The unsaturated nature of the P-V hysteresis loops exhibited by the films prepared on the Ta substrate electrode is strongly linked to the high leakage current effect due to high oxygen vacancies at the Ta/KNO₃ interface, the electronegativity of Ta as well as its partially filled d-shell. The well-defined hysteresis loop exhibited by the films prepared on SS is accounted for by the minimal leakage current effect due to the near absence of oxygen vacancies at the

KNO₃/SS interface. Since SS has some oxygen dissolved in it, it is able to act as an oxygen reservoir that reduces the occurrence of oxygen vacancies at the KNO₃/SS interface. The better performance of KNO₃/Ni over KNO₃/Ta was ascribed to the electronegativity of Ni being higher than Ta and the more filled d-shell of Ni compared with Ta. It is also believed that the level of oxygen vacancies at the Ni/KNO₃ interface due to the elevated temperature deposition reduced injection of electronic carriers into the KNO₃ film, and consequently preventing polarization loss.

The dielectric constant temperature dependence measurements revealed that all the studied samples exhibited a second-order phase transition during the paraelectric-ferroelectric phase transition. The 10³ order of the Curie constant values obtained was a proof that KNO₃ is an order-disorder ferroelectric material. A shift in Curie point T_c was observed for the films prepared on SS while the films prepared on Ni and Ta recorded the inherent T_c of KNO₃. Misfit strain could not be linked to this shift in T_c because of the closely related strains experienced by all the deposited films irrespective of the substrate. From these closely related misfit strains, it was expected that the films prepared on Ni and Ta would also exhibit shifts in their T_c's. This was however not the case because only films deposited on SS showed such characteristics. This occurrence is therefore accounted for by strain resulting from lattice defects. The defects are due to deformations caused by diffused iron (Fe) filling the interstitial sites of KNO₃ due to the possibility of chemical interdiffusion at elevated temperature film depositions. The relatively large ionic radius of iron (Fe) compared to the interstitial sites of KNO₃ being occupied, deformed the lattice of the films prepared on SS. This defect in the lattice consequently caused strain to develop in the film, and thus, shifted the T_c to about 20 °C above the inherent T_c of KNO₃.

The P_s and P_r temperature dependence plots showed that films prepared on all three substrate

electrodes showed a polymorphic transition. During cooling a transformation from phase I into phase III and then into phase II was observed. During heating phase II was observed to transformed into phase III and then into phase I at high temperatures. The P_c and P_r associated with the hysteresis loops attained at maximum polarization were not particularly high for all the studied samples. A P_r value of $2.88 \,\mu\text{C/cm}^2$ was attained by the $1.0 \,\mu\text{m}$ thin film layer prepared on SS and Ni during cooling. On heating, a slightly higher P_r value of $3.30 \,\mu\text{C/cm}^2$ was attained by this $1.0 \,\mu\text{m}$ thin film layer prepared on SS while the $1.0 \,\mu\text{m}$ thin film deposited on Ni reduced slightly to $2.74 \,\mu\text{C/cm}^2$ during heating. It is however significant to note that the stability of the ferroelectric phase was significantly enhanced.

6.2 **Recommendations**

Though this work has shown the possibility of using substrate electrode to stabilize the ferroelectric phase of KNO₃ thin films, more light can be thrown on this finding by investigating other substrate electrodes. Thinner films of deposited KNO₃ can also be investigated to clearly understand the complementary role film thicknesses play in the stability of the ferroelectric phase of thin films of KNO₃. Further work can also be carried out to ascertain why during heating, the ferroelectric phase (phase III) occurred and was sustained even to elevated temperatures of about 170 °C. Structural investigations can be performed by means of x-ray diffraction (XRD) technique to establish how the substrate electrodes might have altered the structural properties of the film and consequently altered the stability of the ferroelectric phase. Microstructural investigations can also be carried out using scanning electron microscopy (SEM) to observe the resulting microstructure of the film after deposition in order to understand how the stability of the ferroelectric phase might have been affected by it.

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Appendices

Appendix A

A.1 P-V Loop and J-V Curve Exhibited by the Ni/KNO₃/Ni, SS/KNO₃/SS and Ta/KNO₃/Ta Thin Film Samples

Figure A.1: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the cooling of the Ni/KNO₃/Ni thin film sample.



Figure A.2: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the cooling of the SS/KNO₃/SS thin film sample.



Figure A.3: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the cooling of the Ta/KNO₃/Ta thin film sample.



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Figure A.4: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the heating of the Ni/KNO₃/Ni thin film sample.



P (nCcm²)

(hycu.s)

Figure A.5: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the heating of the SS/KNO₃/SS thin film sample.



Figure A.6: P-V hysteresis loops and Current density-voltage (J-V) curves exhibited during the heating of the Ta/KNO₃/Ta thin film sample.



Appendix B

B.1 Used Softwares

- LATEX : typesetting and layout
- GNU Image Manipulation Program (GIMP) : graphics
- Microsoft Excel : data processing
- Golden Software Grapher 8 : plots